Novel thienyl dyes
And
Related metal carbonyl complexes

This thesis is presented for the degree of
Doctor of Philosophy
By
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At
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School of Chemical Sciences

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Declaration

I hereby certify that this material, which I now submit for assessment on the programme of study leading to the award of Doctor of Philosophy is entirely my own work, that I have exercised reasonable care to ensure that the work is original, and does not to the best of my knowledge breach any law of copyright, and has not been taken from the work of others save and to the extent that such work has been cited and acknowledged within the text of my work.

Signed: ___________________________  Student number: ________________

Date: _____________________________
Dedication

To the memory of my parents
Acknowledgements

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Quotation

However, until a chemist has separated a gram of porphyrin by column chromatography and seen the purple lustrous crystals made by his or her own hands (and split all over their bench and lab coat, or over the inside of their rotary evaporator), then they really cannot say they’ve worked with porphyrins.

The Colours of Life
Lionel R. Milgrom
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Abstract

Chapter one serves as an introduction to the principles and methods used throughout this thesis. The principles of photophysics are discussed generally and also in relation to porphyrins and dipyrromethenes. Potential applications for the novel thienyl dyes and related metal carbonyl complexes synthesised are then presented. This is followed by an outline of the techniques of laser flash photolysis, time-resolved infrared (TRIR) spectroscopy and time correlated single photon counting.

Chapter two involves the study of thienyl porphyrins. This chapter begins with a literature survey on the synthesis, photophysics and electrochemistry of thienyl porphyrin systems. The synthesis of the porphyrins studied is given, followed by their photophysical and electrochemical properties. The effect of the thienyl moiety on the ground state and excited state properties of the porphyrin macrocycle is examined.

Chapter three commences with a general introduction to Sonogashira-Hagihara type cross coupling reactions and is followed by a literature survey on the synthesis and photochemistry of thienyl based organometallic systems. The synthesis of the novel systems produced for this study is then described and the photophysical properties are examined. Electrochemical data are also presented. The photochemistry of the Co$_2$(CO)$_6$ complexes are examined by steady state photolysis in the presence of a trapping ligand. Three of the complexes were studied by TRIR on a picosecond timescale and the quantum yields of CO loss were determined at a range of excitation wavelengths.

Chapter four commences with a literature survey focusing on the photophysics of pyridyl porphyrins and related organometallic systems. The synthesis of the monopyridyltriphenyl porphyrin and metal carbonyl derivatives produced for this study is described. The photochemistry of the complexes was examined by pump and probe TRIR spectroscopy on a picosecond timescale.

Chapter five contains with a short literature review on the synthesis and photophysics of dipyrromethanes and dipyrrin compounds. The synthesis of a series of substituted thienyl dipyrromethanes, related dipyrrin complexes and corresponding dicobalt complexes is presented. Preliminary photophysical measurements are discussed.

Finally chapter six discusses future work for chapters 3, 4 and 5.
Abbreviations

\( \text{PS}_1 / \text{P}_{700} \) Photosystem I
\( \text{PS}_2 / \text{P}_{680} \) Photosystem II
Chl Chlorophyll
OEC Oxygen evolving complex
Pheo Pheophytin
\( \text{NADP}^+ / \text{NADPH} \) Nicotinamide adenine dinucleotide phosphate
ATP Adenosine triphosphate
LF Ligand Field
IL Intra Ligand
CT Charge Transfer
MLCT Metal to Ligand Charge Transfer
LMCT Ligand to Metal Charge Transfer
CTTS Charge Transfer to Solvent
HOMO Highest Occupied Molecular Orbital
LUMO Lowest Unoccupied Molecular Orbital
BODIPY Borondifluoride dipyrromethene
\( ^3\text{O}_2 \) Ground state oxygen
\( ^1\text{O}_2 \) Singlet excited state oxygen
PDT Photodynamic therapy
ALA \( \delta \)-Aminolevulinic acid
TDPH Tetrapyrrrole-dependant photodynamic herbicides
CO-RM Carbon Monoxide Releasing Molecule
TRIR Time resolved infrared
TRrR Time resolved resonance Raman
TC-SPC Time correlated single photon counting
TAC Time to amplitude convertor
PM1/2 Photomultiplier \( \frac{1}{2} \)
MCA Multichannel pulse analyser
ZnTPP Zinc tetra phenyl porphyrin
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<tr>
<th>Acronym</th>
<th>Definition</th>
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<tr>
<td>ZnTThP</td>
<td>Zinc tetra thienyl porphyrin</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width half maximum</td>
</tr>
<tr>
<td>IRF</td>
<td>Instrument response function</td>
</tr>
<tr>
<td>SCE</td>
<td>Saturated calomel electrode</td>
</tr>
<tr>
<td>STM</td>
<td>Scanning Tunneling Microscopy</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium tin oxide</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission emission spectroscopy</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>DM-β-CD</td>
<td>Dimethoxy-β-cyclodextrin</td>
</tr>
<tr>
<td>TM-β-CD</td>
<td>Trimethoxy-β-cyclodextrin</td>
</tr>
<tr>
<td>O$_2^-$</td>
<td>Superoxide anion radical</td>
</tr>
<tr>
<td>IPCE</td>
<td>Incident photon-to-current efficiency</td>
</tr>
<tr>
<td>$\eta_{\text{max}}$</td>
<td>Maximum power conversion efficiency</td>
</tr>
<tr>
<td>TM-SFM</td>
<td>Tapping-mode scanning force microscopy</td>
</tr>
<tr>
<td>fs-HRS</td>
<td>Femtosecond – hyper Rayleigh scattering</td>
</tr>
<tr>
<td>β</td>
<td>Molecular first hyperpolarisability</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>FT-IR</td>
<td>Fourier transform – infrared</td>
</tr>
<tr>
<td>ppm</td>
<td>Parts per million</td>
</tr>
<tr>
<td>$J$</td>
<td>Coupling constant</td>
</tr>
<tr>
<td>NLO</td>
<td>Non linear optics</td>
</tr>
<tr>
<td>OTE</td>
<td>Oligo(2,5-thienylethynylene)</td>
</tr>
<tr>
<td>ICT</td>
<td>Intramolecular charge transfer</td>
</tr>
<tr>
<td>$\text{H}_{\text{ECC}}$</td>
<td>Effective conjugation length</td>
</tr>
<tr>
<td>$R_g$</td>
<td>Radius of gyration</td>
</tr>
<tr>
<td>PL</td>
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<td>ETB</td>
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Chapter 1

Introduction

Chapter one serves as an introduction to the principles and methods used throughout this thesis. The principles of photophysics are discussed generally and also in relation to porphyrins and dipyrrromethenes. Potential applications for the novel thienyl dyes and related metal carbonyl complexes synthesised are then presented. This is followed by an outline of the techniques of laser flash photolysis, time-resolved infrared (TRIR) spectroscopy and time correlated single photon counting.
1.1 Principles of photophysics

The absorbance of a photon of light, with energy $h\nu$, by a molecule generally causes a valence electron in the absorbing species to be promoted to an orbital of higher energy and results in the formation of an electronically and vibrationally excited state of that particular species (Rxn. 1). This excited state species can then decay back to the ground state through spontaneous emission (Rxn. 2) or through stimulated emission (Rxn. 3). The spontaneous downward transition of an excited state electron can occur by emission of light (radiative decay) or by conversion of the excess energy into heat (non-radiative decay).

\[
\text{Rxn. 1} \quad M + h\nu \rightarrow M^* \\
\text{Rxn. 2} \quad M^* \rightarrow M + h\nu \\
\text{Rxn. 3} \quad M^* + h\nu \rightarrow M + 2h\nu
\]

These ground and excited “states” are defined by the distribution of all nuclei and all electrons within the molecule, the wave function of the molecule. Electrons have much less inertia than nuclei; consequently they can adjust their position and motion almost instantaneously. Since the motions of electrons in orbitals are much more rapid than nuclear motion, electronic and nuclear motions can be treated separately in terms of an approximate wave function. This separation of nuclei and electrons is known as the Born-Oppenheimer approximation and assumes that the heavy nuclei remain motionless while the light electrons move around them.

Electronic motions occur at a faster timescale ($< 10^{-13}$ s) than nuclear motion ($10^{-11} - 10^{-13}$ s); as a result nuclei remain essentially stationary during an electronic transition (absorbance or emission). This is the Franck-Condon principle.\(^1\) For this reason when a molecule in its ground state absorbs a photon it forms a metastable excited electronic configuration (Franck-Condon excited state) where the nuclear geometry is characteristic of the ground state. Following the production of this Franck-Condon excited state, rapid
vibrational relaxation to the lowest vibrational level of the electronic excited state occurs producing a thermally and vibrationally equilibrated excited state on a time scale of the order $10^{-12}$ s. This equilibrated excited state is known as a “thexi” state. Thexi states have a definite chemical structure, chemical reactivity and absorbance spectrum and hence can be considered as excited state isomers of the ground state.

There are several relaxation pathways by which such thexi states can return to their ground state and knowledge of these pathways is essential to understanding the photophysics and photochemistry of the molecule. On formation of the high energy singlet ($S_n$) or thexi state vibrational relaxation can occur to a lower excited state by internal conversion or intersystem crossing. Internal conversion is the non-radiative relaxation to a lower excited state and occurs between states of the same multiplicity ($S_n \rightarrow S_1$, $S_1 \rightarrow S_0$, and $T_n \rightarrow T_1$, where $n > 1$). Intersystem crossing is the non-radiative decay between two states of different multiplicity ($S_1 \rightarrow T_1$).

Radiative decay to the ground state (luminescence) can also take place when an excited state molecule loses its excitation energy as a photon of light. This emission of light occurs as either fluorescence or phosphorescence. Fluorescence is caused by the decay between states of the same multiplicity ($S_1 \rightarrow S_0$), whereas phosphorescence is a result of decay between states of different multiplicity ($T_1 \rightarrow S_0$). In accordance with Kasha’s rule, emission occurs only from the lowest energy excited state of the molecule. Therefore, as with the initial Franck-Condon excited state, vibrational relaxation to the lowest energy excited state must occur by rapid internal conversion before emission can proceed. It is the efficiency with which internal conversion or intersystem crossing takes place that controls the type of emission. Differentiation between the two luminescence processes is possible as each emission occurs on a different timescale. These transitions are illustrated in figure 1.
As emission from the $S_1 \to S_0$ level is spin allowed fluorescence is spontaneous and short lived with lifetimes generally in the range 1 ps – 1 µs. Vibrational relaxation to the first excited singlet state prior to emission consumes energy such that when radiative emission occurs it is at lower energy than the absorbed radiation. This re-emission of less energetic photons, which have longer wavelengths than the absorbed photons, is known as a Stokes shift (Fig. 2, a). Often the fluorescence spectrum is a mirror image of the absorbance spectrum. At room temperature it is typically the $v = 0$ vibrational level of the $S_0$ ground state that is populated, so excitation following absorbance is from the $v = 0$ of $S_0$ to any vibrational level of $S_1$. The return fluorescence begins in the $v = 0$ level of $S_1$ to the various vibrational levels of $S_0$ resulting in the mirror image (Fig. 2, b).
Phosphorescence, emission from T₁ → S₀, is considered “spin forbidden” and takes place on a much slower time scale ranging from 1 µs to many seconds. As the T₁ state is lower in energy than the S₁ state phosphorescence occurs at longer wavelengths than fluorescence. The processes of intersystem crossing and phosphorescence are both spin-forbidden but can occur where there is spin-orbit coupling. Intersystem crossing can proceed where vibrational coupling between the singlet excited state and triplet excited state occurs. Spin-orbit coupling increases with increasing atomic number thereby enhancing the rates of formally spin forbidden processes. This is known as the heavy atom effect. As a result of the heavy atom effect a decrease in fluorescence quantum yield and an increase in triplet quantum yield are observed, together with a decrease in triplet lifetime (phosphorescence).¹

The electron distribution of a molecule is primarily what determines its reactivity. In the excited state, the electron distribution is changed with respect to the ground state thus the reactivity has also changed. Molecular orbital theory is used to describe electronic transitions in terms of localisation of electron density from origin to destination. Such transitions include:

---

¹ For further details on heavy atom effects, see Ref. [1].
1. **Ligand-Field (LF) d-d transitions**

   These excited states are usually called *d-d transitions* as the excited state arises from electron transitions between metal d orbitals. Such transitions result in an angular rearrangement of electron density, with no change in distribution between ligands and metal. The angular rearrangement of the metal electron has little effect on internal redox processes (i.e. towards the homolytic fission of metal–ligand bonds) but has important consequences in changing the reactivity of the metal towards ligand substitution or isomerisation reactions. The excitation of an electron from a metal orbital directed away from the ligand to an orbital directed towards a ligand can cause: an increase in metal to ligand repulsion with lengthening of the metal to ligand bond distance and subsequent detachment or nucleophilic attack of the metal.

2. **Intra-ligand transitions (IL)**

   Electron transitions between two molecular orbitals primarily centred on the ligand orbital give rise to intra-ligand transitions, also called *ligand centred transitions*. These transitions do not affect the charge distribution between the ligands and metal or the bonding structure of the complex directly. They may however change the donor-acceptor properties, dipole moment of the excited state species.

3. **Charge-transfer transitions (CT)**

   These are transitions between molecular orbitals centred on the metal and molecular orbitals centred on the ligands and are sometimes referred to as *electron transfer transitions*. The charge transfer transitions can be further subdivided into *metal to ligand* (MLCT; d-π*) and *ligand to metal* (LMCT; σ or π-d) charge transfer depending on where the excited electron originates. These transitions cause the radial redistribution of the electron density between the central metal and ligands. Charge transfer excited states increase the reactivity towards substitution reactions as the oxidation state of the metal is changed. MLCT transitions increase the positive charge on the metal facilitating nucleophilic attack by other ligands. In LMCT transitions the electron is generally transferred into an antibonding metal orbital. Transitions to the solvent medium can occur. Charge transfer from a metal centred orbital to a solvent orbital is called *charge transfer to solvent* (CTTS).
1.2.1 Porphyrins

Porphyrins are a large class of pigments known for their intense purple colour. The basic structure, first proposed by Kuster in 1912, consists of a large macrocycle containing 20 carbon atoms and four nitrogen atoms.\(^3\) The atoms are arranged as four pyrrole units linked through \(\alpha\) and \(\alpha'\) positions by four methine bridges. The first synthetic porphyrin to be reported was the “heme” porphyrin, containing an iron at its core.

The most basic, unsubstituted porphyrin is called porphine (Fig. 3, a) and its structure is the basic skeleton that all other porphyrins possess. There are two types of substituted porphyrin: \(\beta\) substituted porphyrins (Fig. 3, b), which have one or more substituents on the pyrrole rings (all naturally occurring porphyrins are of this type) and meso substituted porphyrins (Fig. 3, c), which have substituents attached to the methine bridge (the meso position). The majority of synthetically produced porphyrins are the latter type. Highly substituted or over crowded porphyrins have substituents at both the \(\beta\) and meso positions.\(^4\)

![Figure 3 Basic structure and substitution pattern of porphyrins (R = alkyl or aromatic substituents)](image)

Porphyrons that contain two internal protons (N-H protons) are referred to as freebase porphyrins. These protons on the central nitrogens are weakly acidic (\(pK_a \approx 16\)) and can be readily displaced by various metals (Zn, Mg, Cu, Ni, Pd) to yield the corresponding metalloporphyrin (Rxn. 4). Metalloporphyrins can be split into two classes: regular and irregular and are discussed below.

\[
\text{Rxn. 4} \quad \text{H}_2\text{P} + \text{M}^{2+} \leftrightarrow \text{MP} + 2\text{H}^+ 
\]
1.2.2 Properties of porphyrins

The porphyrin system consists of 22 $\pi$ electrons, 18 of which are delocalised over the macrocycle. Hence, porphyrins are aromatic molecules as they obey Hückel’s rule of aromaticity ($4n + 2\pi$ electrons, where $n = 4$). X-ray crystallography has shown that porphyrins are planar molecules (all atoms are in sp$^2$ configuration) while heat of combustion experiments also confirmed aromaticity.

The aromatic nature of porphyrins can also be observed in the $^1$H NMR signals. The two endocyclic protons (N-H protons) are shielded by the aromatic ring current and their resonance is shifted to a high field position, beyond TMS, typically between -2 and -4 ppm. Upon displacement of the internal protons by a metal ion the high field signal is no longer observed. The diamagnetic ring current also affects the external protons at the $\beta$ and meso positions. In this case, the deshielding effect causes a downfield shift in resonances for these protons.

Perhaps the most distinctive feature of a porphyrin is its UV-visible spectrum. The spectrum consists of two distinctive regions: the B or Soret band region and the Q band region, which occur in the near ultraviolet and visible parts of the electromagnetic spectrum respectively (Fig. 4). A strong transition to the second excited state ($S_0 \rightarrow S_2$) known as the “B” (strongly allowed) or “Soret” band usually occurs between 390 – 430 nm and is the most intense absorbance in the spectrum having molar extinction coefficients of the order $10^5$ $\text{M}^{-1}\text{cm}^{-1}$. Two weak transitions to the lowest excited singlet state ($S_0 \rightarrow S_1$) are commonly referred to as the “Q” bands ($Q$ – quasi allowed). They are in the lower energy region of the spectrum, generally observed between 500 – 700 nm. Metalloporphyrins give rise to two Q bands as they possess $D_{4h}$ symmetry whereas the less symmetrical freebase porphyrins, with $D_{2h}$ symmetry, display four Q bands. In metalloporphyrins, the lowest energy transition, sometimes referred to as $\alpha$, is denoted Q(0,0) and arises from the lowest energy excited singlet state. The higher energy band, sometimes referred to as $\beta$, is a vibrational satellite of the Q(0,0) band and is denoted Q(1,0). When the central metal is replaced by two hydrogens, as in freebase porphyrins, the reduction in symmetry causes a splitting of the Q bands, where the Q(0,0) splits into Q$_x$(0,0) and Q$_y$(0,0) and its vibrational overtone Q(1,0) splits into Q$_x$(1,0) and Q$_y$(1,0) thus doubling the number of Q bands to four.$^4$
Metalloporphyrins can be categorised as either regular or irregular and display three types of absorbance spectra called normal, hypso and hyper, where the effects of the interaction of the metal and porphyrin orbitals is observed. Regular metalloporphyrins display normal absorbance and emission spectra which are largely determined by the porphyrin π electrons as the central metal has very little interaction with the porphyrin orbitals. However a decrease in the fluorescence of regular metalloporphyrins is observed in accordance with the heavy atom effect. In irregular metalloporphyrins there is extensive interaction between the porphyrin π electrons and the electrons of the central metal ion. Irregular porphyrins produce hypso and hyper absorbance spectra. Hypso absorbance spectra are hypsochromically shifted with respect to normal porphyrins and hyper absorbance spectra display prominent additional absorbance bands in the region λ > 320 nm. The position of the Q bands also relies on the central metal and whether it has any axial ligands.\(^4\)
Gouterman et al. developed the four-orbital model to illustrate how the Soret and Q bands arise from porphyrin $\pi$-$\pi^*$ transitions (Fig. 5). The absorbance bands of porphyrin systems arise from transitions between two HOMOs and two LUMOs. The $\pi$ orbitals are two non-degenerate orbitals labelled $a_{2u}$ and $a_{1u}$ for HOMO and HOMO-1 respectively, while the LUMO $\pi^*$ orbitals are two degenerate orbitals labelled $e_g$. For *porphine*, the electronic configuration of the ground state is $^1A_{1g}$ comprised of ($a_{1u}^2 a_{2u}^2$). The lowest excited singlet state configurations are $^1(a_{2u}^1 e_g^1)$ and $^1(a_{1u}^1 e_g^1)$. The degenerate nature of these singlet states causes strong configurational interaction between them. Mixing of the transition dipoles of the two configurations in a constructive manner results in the intense Soret B(0,0) band, while mixing of transition dipoles in a deconstructive manner corresponds to the relatively weak Q(0,0) band. The closer the degeneracy of the ($a_{2u}^1 e_g^1$) and ($a_{1u}^1 e_g^1$) configurations, the weaker the Q(0,0) band becomes. In freebase porphyrins, the symmetrical axis along the internal protons lifts the degeneracy of the $e_g$ ($\pi^*$) orbital causing the Q(0,0) band of the metalloporphyrin to split into $Q_x(0,0)$ and $Q_y(0,0)$ each with a vibronic overtone.

![Figure 5](image-url)  
*Gouterman's four orbital model.*
1.3.1 Dipyrromethenes

Dipyrromethenes, also called dipyrrins, are formally composed of a pyrrole ring and an azafulvene attached through the α positions by a methine bridge (Fig. 6, a and b). A dipyromethane has one less degree of unsaturation possessing a methylene bridge (Fig. 6, c). Similar to porphyrins, they can be substituted at the β pyrrolic position or the meso position on the bridge (Fig. 6).

![Figure 6](image1.png)

*Figure 6*  
(a) β substituted dipyrromethene (b) meso substituted dipyrromethene and (c) basic structure of dipyromethane. (R = alkyl or aromatic substituent).

Dipyrromethenes readily coordinate to divalent metals (M = Zn, Co, Cu, Ni and Pt) to give homoleptic bis(dipyrrinato)metal complexes similar to porphyrins (Fig. 7, a). Dipyrrins can also easily undergo fluoroboration to coordinate with a boron atom to form 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene dyes (Fig. 7, b). They are commonly referred to as borondifluoride dipyrromethenes or BODIPY dyes since their commercialisation.

![Figure 7](image2.png)

*Figure 7*  
(a) Bis(dipyrrinato)metal complex where M = Zn, Co, Cu, Ni, Fe and Pt  
(b) borondifluoride dipyrrin
1.3.2 Properties of borondifluoride dipyrrins

Borondifluoride dipyrrins are flat bipyrrolic structures linked by a BF$_2$ group. Quantum mechanical calculations and X-ray crystallography have confirmed the planar structure of the molecule. In its most basic unsubstituted form, the dye possesses C$_{2v}$ point symmetry. BODIPY dyes are neutral molecules, however, they have a zwitterionic structure where a positive charge is delocalised throughout the $\pi$-system. It was first proposed that the boron atom has a net positive charge due to the electronegative nature of both the fluorine and nitrogen atoms linked to it. However quantum mechanical calculations have shown the negative electronic density of the molecule localised mainly on the F atoms and to a lesser extent the N atoms. The resonance structures are shown in figure 8. The BF$_2$ group does not take part in the delocalised $\pi$-system but instead gives rigidity to the structure. Thus borondifluoride dipyrrromethenes can be classified as quasi-aromatic molecules.

![Resonance structures of borondifluoride dipyrrromethenes.](image)

*Figure 8* Zwitterionic structures of borondifluoride dipyrrromethenes.

BODIPYs possess excellent photophysical properties such as high absorbance coefficients (molar extinction coefficients are of the order $10^5$ M$^{-1}$ cm$^{-1}$) and high fluorescence
quantum yields (typically Φ = 0.7). Their optical properties are easily manipulated by modification of the pyrrole core, the meso position and the boron substituents. The absorbance and emission maxima occur at wavelengths in the range 480-700 nm but vary with substituents (Fig. 9). A strong absorbance in the green part of the visible spectrum, at approximately 500 nm, is attributed to the π-π* transition from the ground state to the first excited state (S₀ → S₁) of the molecule. The shoulder observed at higher energy is assigned to an out-of-plane vibration of the aromatic C-H skeleton. Less intense absorbance bands located in the range 350-400 nm can be attributed to π-π* transitions from the ground state to higher excited states (S₂ or higher).

The intense fluorescence of these compounds has become their most recognised property. The fluorescence spectrum is generally the mirror image of the absorbance spectrum with a weak Stokes shift (~500 cm⁻¹). The shape and position of the fluorescence band is independent of excitation wavelength, in keeping with singlet emitting states and excitation spectra generally match absorbance spectra allowing for the conclusion that emitted light is from the singlet excited state. Substitution of the BODIPY framework can lead to large shifts of their spectral properties and increase the quantum yield close to unity. The fluorescence decay curve of the dyes can be analysed by mono-exponential decay with lifetimes typically in the nanosecond range.

![Absorbance spectrum and corresponding emission spectrum of a substituted phenyl borondifluoride dipyrromethene in CH₂Cl₂.](image)

**Figure 9** Absorbance spectrum and corresponding emission spectrum of a substituted phenyl borondifluoride dipyrromethene in CH₂Cl₂.
1.4 Singlet oxygen

Molecular oxygen in its ground state has triplet multiplicity, $^3\Sigma_g^-$. Excitation causes rearrangements of the electron spins within the degenerate orbitals and results in two possible singlet states, $^1\Delta_g$ and $^1\Sigma_g^+$, above the triplet state. The electronic configurations of these excited states differ only by the electron configuration in the $\pi$ antibonding orbitals (Fig. 10). The transition from the first excited state to the ground state $^1\text{O}_2 (^1\Delta_g) \rightarrow ^1\text{O}_2 (^3\Sigma_g^-)$ is spin forbidden and as such $^1\Delta_g$ state is short lived as it is a spin allowed transition and occurs with almost unit efficiency. Being spin and symmetry forbidden, the metastability of $^1\Delta_g$ state allows the direct observation of the $^1\Delta_g \leftrightarrow ^3\Sigma_g^-$ transition in both the absorbance and emission spectra.\(^8\)

![State Orbital Assignment](image)

**Figure 10** Representation of molecular oxygen lowest triplet and singlet states.

Deactivation of singlet excited state oxygen by other species to return to its ground state can occur in two ways: physical quenching where excited singlet state oxygen is deactivated without oxygen consumption or product formation (Rxn. 5) or chemical quenching where a “quencher” reacts with the singlet oxygen and new products are formed (Rxn. 6). Singlet excited state oxygen is more oxidising than ground state oxygen and therefore is more electrophilic. Owing to the high reactivity of $^1\text{O}_2$ with substrates, the chemistry of $^1\text{O}_2$ has been extensively studied. Typical reactions include oxidations of alkenes (ene-type reactions, [2+2] cycloadditions), 1,3-dienes ([4+2] cycloadditions), aromatic compounds and heterocycles.\(^8\)
\[ Rxn.\ 5 \quad ^1\text{O}_2 + A \rightarrow ^3\text{O}_2 + A \]

\[ Rxn.\ 6 \quad ^1\text{O}_2 + Q \rightarrow P \]

where A = atoms/ molecules that encounter singlet oxygen, Q = quencher and P = product.

The main method of production of \(^1\text{O}_2\) is by photosensitisation reactions, the requirements for which are oxygen, light of appropriate wavelength and a photosensitiser capable of absorbing and using that energy to excite oxygen to its singlet state. Sensitiser excitation is typically achieved via a one photon transition from the ground state, \(S_0\), to a singlet state, \(S_n\), followed by relaxation to the lowest excited singlet state, \(S_1\), with subsequent intersystem crossing to generate the sensitiser triplet excited state, \(T_1\). As discussed previously, the triplet state lifetime is longer (\(\mu\)s) than that of the singlet state lifetime (ns), thus allowing the photosensitiser triplet excited state to react with molecular oxygen. This occurs in two ways, defined as Type I and Type II, according to the nature of the quencher (Fig. 11). Type I involves hydrogen-atom abstraction or electron transfer between the excited sensitiser and a substrate to give free radicals. These free radicals can then react with oxygen to form an active oxygen species, i.e. superoxide radical anion (Fig. 12, Rxn. 7). Type II involves energy transfer during a collision from the excited sensitiser to triplet oxygen to generate singlet oxygen (Fig. 12, Rxn. 8).

\[ \text{Photosensitiser} \]

\[ \text{Type I} \quad \text{Radicals or radical ions} \]

\[ ^3\text{O}_2 \]

\[ \text{Products of Oxidation} \]

\[ \text{Type II} \quad ^3\text{Photosensitiser}^* \quad ^3\text{O}_2 \quad ^1\text{O}_2 \]

\[ \text{Products of Oxidation} \]

*Figure 11 Two pathways (Type I and Type II) of molecular oxygen sensitisation.*
Generally a photosensitiser molecule can produce $10^3 - 10^5$ molecules of $^{1}\text{O}_2$ before being degraded through photobleaching or photodegradation by $^{1}\text{O}_2$. Photodegradation refers to the process in which singlet oxygen reacts with a material resulting in its degeneration, while photobleaching refers specifically to the degradation of dyes by singlet oxygen. The quantum yield of singlet oxygen formation, $\Phi_\Delta$, is dependent on the quantum yield of the triplet state of the sensitiser, $\Phi_T$, though competing reactions must be considered (Fig. 12, Rxn. 9). These include monomolecular radiative and non-radiative processes (Fig. 12, Rxn. 10 and 11) and bimolecular reactions such as physical deactivation by molecular oxygen or electron transfer (Fig. 12, Rxn. 12 and 13). Quenching of the excited state sensitiser by molecular oxygen through electron transfer processes (Fig. 12, Rxn. 13) yields the superoxide radical anion (Type I quenching).

![Figure 12](image)

**Figure 12**  Singlet oxygen production and processes affecting yield and efficiency, where Sens = sensitisier, $Q$ = quencher, $K_{en}$ = rate of energy transfer, $S_\Delta$ = fraction of triplet molecules quenched by oxygen and yielding singlet oxygen, $S_q$ = fraction of oxygen dependant triplet deactivations, $K_r$ = rate of radiative decay, $K_{nr}$ = rate of nonradiative decay, $K_{dO_2}$ = rate of deactivation by $O_2$ and $K_{et}$ = rate of electron transfer.
Typically photosensitisers are divided into three categories: organic dyes and aromatic hydrocarbons, porphyrins and other porphyrinoid compounds, and transition metal complexes. Photosensitisers should exhibit the following properties (1) high extinction coefficients in the spectral region of excitation; (2) a triplet state with appropriate energy to allow efficient energy transfer to ground state oxygen; (3) long lived triplet state lifetimes ($\tau_T > 1 \mu s$) with high quantum yields ($\Phi_T > 0.4$); and (4) high photostability. Porphyrins and their derivatives have the ability to absorb several wavelengths in the UV-vis spectrum and they also possess long lived triplet states that allow for high quantum yields. Substitution around the macrocycle, coordination of metal ions at its centre and axial ligation of the central metal ion allow for the tuning of the photophysical properties of porphyrins. Aggregation of the photosensitiser is not desirable as photodynamic efficiency decreases due to the decreased sensitising ability of dimers and higher aggregates. Aggregation can be circumvented by bulky substituents on the periphery of the porphyrin macrocycle.

Singlet oxygen has found application in areas such as waste water treatment\(^9\) and fine chemical synthesis\(^{10}\) and in photodynamic processes. The photodynamic effect is the damage caused to living tissue by the combination of a photosensitiser, light and oxygen. Due to the rapid reaction of singlet oxygen with biomolecules, direct spectroscopic evidence of singlet oxygen in photodynamic therapy (PDT) is difficult to find. It is generally accepted the $^1\text{O}_2$ ($^1\Delta_g$) is the major participant.\(^{11}\)

Blood sterilisation, but more specifically, decontamination of freshly frozen plasma units is carried out using PDT.\(^{12}\) Methylene blue is known for its lack of toxicity to humans and is an effective photosensitiser in destroying extracellularly-enveloped viruses. Silicon-based phthalocyanines are also under investigation for sterilisation of blood components.\(^{13}\)

Photodynamic therapy is a relatively new type of cancer treatment.\(^{12}\) In PDT of cancer, a photosensitiser, visible light and oxygen are combined to produce lethal agents which destroy or inactivate tumour cells. In is widely agreed that singlet oxygen is the primary
cytotoxic agent responsible for the photobiological activity. The dual selectivity of PDT arises from the preferential accumulation of photosensitiser in diseased tissue and the ability to confine activation of the photosensitiser by illumination of the tumour region only. This allows for tumour destruction without effecting normal healthy tissue. The majority of sensitisers investigated to date are of porphyrinoid structure.\textsuperscript{14} First generation photosensitisers included haematoporphyrin derivative (HpD) and its analogues, which were the first compounds to be authorised for clinical use. These PDT agents were a mixture of about ten components. Poor selectivity, long retention times and poor reproducibility of biological effects meant a second generation of photosensitisers was required. This second generation of PDT sensitisers were structurally distinct compounds with long wavelength absorbance. Third generation photosensitisers use second generation photosensitisers bound to carriers for a higher selective accumulation in the tumour.\textsuperscript{8}

In a similar manner photodynamic herbicides and insecticides use the toxic effects of singlet oxygen to destroy unwanted plants or pests. Photodynamic herbicides cause the accumulation of chlorophyll and heme metabolic intermediates (tetrapyrroles) in green plants.\textsuperscript{15} These accumulated tetrapyrroles, once exposed to light, act as photosensitisers for the production of singlet oxygen which kills the treated plants through oxidation of their tissues while leaving untreated plants unharmed. \(\delta\)-Aminolevulinic acid, (ALA), is the main precursor of all tetrapyrroles in plant and animal cells and as such the main component in these tetrapyrrole-dependant photodynamic herbicides (TDPH). The insecticidal effects of photosensitisers have also been studied.\textsuperscript{16} Organic dyes, such as xanthenes, were extensively examined for this purpose. They possess the high photosensitising capabilities required and their poor photostability is in fact advantageous. Persistence of conventional insecticides in the environment is a serious issue but is eliminated by the facile decomposition of xanthene dyes. More recently porphyrin-based insecticides have been investigated. These compounds can be activated by a range of wavelengths and have shown to be effective as insecticides.
1.5 Carbon monoxide – releasing molecules (CO-RMs)

Carbon monoxide (CO) is widely considered to be an environmental poison but CO, like nitric oxide (NO), elicits essential biological functions in humans when formed in discrete quantities. Akin to the change in attitude towards NO, the reputation of CO as a noxious polluting gas is changing to that of a vital messenger molecule important for processes in all living organisms. In high concentrations the toxic effects of carbon monoxide are typified at biological levels by the high affinity of CO for haemoglobin and cytochromes, both of which carry out oxygen transport and mitochondrial respiration. However at low concentrations CO can be utilised for therapeutic purposes in the resolution of various pathological states. CO has been shown to regulate vessel tone and blood pressure, exert anti-inflammatory actions, inhibit platelet aggregation and suppress rejection of transplanted hearts. Heme is oxidised at the α-position of the protoporphyrin ring by heme oxygenase to generate ferrous iron, carbon monoxide and biliverdin. Two isoforms of heme oxygenase exist (HO-2 and HO-1) suggesting that the cells have evolved to regulate heme consumption and ultimately the production of CO. Basal production of carbon monoxide in humans is estimated to be 6 µmol Kg$^{-1}$ day$^{-1}$ and this rate increases significantly in pathological states such as asthma, cystic fibrosis and diabetes as the body responds to counteract these conditions. Therefore the development of Carbon Monoxide – Releasing Molecules (CO-RMs) should be emphasised as encouraging prospects for therapeutic agents.

While some main group elements have been shown to bind and release CO, the obvious choice for CO-releasing molecules are transition metal complexes with one or more carbon monoxide ligands. Mann and Motterlini have created the foundations in this area, by demonstrating that some homoleptic and non-homoleptic transition metal carbonyl complexes can act as CO-RMs in biological systems. Metal carbonyl complexes should satisfy some essential prerequisites for later in vivo applications including reasonable water solubility, controlled release of CO ligands with known follow up products (simple CO exchange or further reaction) and non-toxicity prior to and after decomposition.
The bonding in metal carbonyls will be discussed in detail in chapter three. For the purposes of carbon monoxide release, dissociation of CO from metal complexes is a result of the cleavage of the metal carbonyl (M-CO) bond. Consequently a relatively weak M-CO bond is favourable. There are several different approaches for potential CO delivery. Photochemical cleavage using smooth light irradiation in order to promote CO release has been examined, though this technique has limited applications at sites which are not directly exposed to the body’s surface. The use of prodrugs (i.e. methylene chloride) that are catabolised by hepatic enzymes to generate CO have been examined. Also under investigation is the transport and delivery of CO by means of specific CO carriers. The chemistry of transition metals allows them to be effectively modified by coordination of biological ligands to the metal centre in order to render the molecule less toxic and more water soluble while modulating the liberation of CO. While this research is still in its infancy, complexes that have been characterised as potential CO-RMs include those that contain a heavy metal such as nickel, cobalt or iron surrounded by carbonyl (CO) groups as coordinated ligands. Studies have shown that certain ligands in a metal complex can promote, either electronically or sterically, dissociation of CO. The extent and rate of CO release from CO-RMs is assessed by measuring the conversion of deoxy myoglobin to myoglobin-CO. Motterlini et al. also discovered that the rate of CO release from CO-RMs, which can be fine tuned to achieve fast or slow release, allows the modification of the ensuing biological effect. The complexes, [Fe(CO)₅], dinuclear [Mn(CO)₁₀] and [{Ru(CO)₃Cl₂}]₂ were among the first complexes reported to release carbon monoxide in biological models and also to promote relaxation of blood vessels in vitro.

In organometallic chemistry, substitution by loss of CO is a common feature though it is rarely studied in aqueous media. Further studies are necessary to elucidate the full requirements for effective CO release and to understand the delicate balance between CO liberation and CO-RM stability. Limited numbers of CO-RMs have been examined. Thus the development of new molecules or complexes which release CO under physiological conditions at specific sites needs to be further investigated. It is also likely that many CO releasing molecules synthesised for other uses (i.e. as catalysts in organic synthesis) may possess the properties required of a CO-releasing molecule in biological systems.
1.6.1 Laser flash photolysis

The technique of laser flash photolysis was developed by Norrish and Porter during the 1950’s.\textsuperscript{24} They were awarded the Nobel Prize in 1967 for their studies of extremely fast chemical reactions. Using very short pulses of energy to disturb the equilibrium, observation of short-lived intermediates present in photochemical processes was possible.

The fundamental technique of laser flash photolysis involves irradiation of a sample with a high intensity pulse of light (e.g. laser or discharge lamp) within a very short time, which produces a high concentration of excited state species (transient species, radical or photoproduct) in that time interval. With its short pulse duration, high intensity and monochromatic nature, laser radiation is ideal for this purpose. By monitoring the evolution of the system in time using UV-vis or IR detection, the reaction kinetics can be determined.

Using UV-vis detection, the changes in the absorbance of an excited state transient species as it undergoes thermal relaxation to the parent compound can be observed. However for UV-vis detection to be viable there are two factors that must be considered. Primarily, the thermal relaxation of the excited state must occur on a longer timescale than the lifetime of the laser pulse itself. Secondly, the excited state absorbance spectrum must be sufficiently different from the parent compound so that the changes can be observed. Well resolved characteristic absorbance spectra aid the identification of intermediates whereas transient species with low molar extinction coefficients may not be detected.

A significant disadvantage of UV-vis monitored laser flash photolysis is the lack of structural information available for a particular system. However when coupled with time-resolved infrared (TRIR) and time-resolved resonance Raman (TRrR) spectroscopy it becomes a much more comprehensive technique. The infrared spectrum of metal carbonyls observed in the carbonyl stretching region (1700 – 2200 cm\textsuperscript{-1}) allows structural information to be obtained. The number and intensity of the infrared bands, which is dependent on the molecular symmetry, provide a direct signal as to the geometry of a molecule.
1.6.2 Laser flash photolysis with UV-vis detection

A schematic diagram of the laser flash photolysis instrumentation is given in figure 13. The excitation source is a neodymium yttrium aluminium garnet (Nd:YAG) laser, which operates at a frequency of 1064 nm. The host YAG crystals are implanted with Nd atoms of approximately one part per hundred. The main advantage of the YAG host material is its relatively high thermal conductivity which removes wasted heat, thus allowing these crystals to operate at high repetition rates of many pulses per second. Using non-linear optics, the fundamental frequency of 1064 nm can be doubled, tripled or quadrupled to generate a second, third or fourth harmonic frequency at 532, 355 or 266 nm respectively. This allows specific excitation pathways within a system to be selected. Amplification of the laser power can be carried out by varying the voltage across an amplifier flash tube. At a frequency of 355 nm, the energy generated is typically 45 mJ per pulse and the lifetime of the laser pulse approximately 10 ns.

The circular laser pulse is diverted *via* a Pellin Broca prism through an optical trigger (which prepares the transient digitiser) onto the sample cuvette. The transient digitiser (a Hewlett Packard HP 54510A oscilloscope) detects the transient species. Positioned at right angles to the laser beam is the monitoring light source, is an air-cooled 275 W Xenon arc lamp that monitors any changes induced in the sample. Throughout the experiment UV-vis filters are employed between the Xenon arc lamp and the sample to prevent excessive photodegradation. After passing through the sample the monitoring beam is directed to the entrance slit of an Applied Photophysics f/3.4 monochromator *via* a circular lens. A Hamatsu 5 stage photomultiplier operating at 850 V is situated at the exit slit of the monochromator. Following activation of the optical trigger the transient digitiser (oscilloscope) measures changes in the absorbance *via* a variable load transistor.
A typical transient signal is obtained in the following manner: Initially the amount of monitoring light being transmitted through the sample solution prior to the laser flash, $I_0$, is recorded. $I_0$ (mV) is the voltage corresponding to the amount of light detected by the photomultiplier tube when the Xenon arc lamp shutter is open less the voltage generated by stray light when the shutter is closed. While firing the laser, the Xenon arc lamp shutter is simultaneously opened, allowing the laser pulse to pass through the sample cuvette and the amount of light transmitted to be recorded ($I_t$). According to the Beer – Lambert law absorbance = log ($I_0/I_t$). The change in intensity of the monitoring beam transmitted through the sample is measured as a function of time and/or wavelength. Therefore a typical trace depicts the change in absorbance/voltage with time. The time-resolved absorbance may then be analysed by first or second order kinetics. Transient absorbance difference spectra are obtained as a result of point by point build up by changing the wavelength of the monochromator (usually every 10 nm) with consistent time-base and voltage settings. Solvents of spectroscopic purity are required to limit impurities while sample solutions must also be optically transparent for the monitoring beam. A general procedure describing sample preparation for laser flash photolysis experiments is given in appendix A.

Figure 13  Schematic diagram of laser flash photolysis instrumentation.
1.6.3 Time resolved infrared spectroscopy

While time resolved optical spectroscopy allows the elucidation of kinetic information from a transient species, the broad and often featureless absorbance bands observed in the UV-vis following excitation give little structural information. For this reason time resolved infrared (TRIR) spectroscopy is a very complementary technique. TRIR spectroscopy involves the direct observation of transient species evolving over time using IR detection. Laser flash photolysis is used to generate the intermediates in solution while ultra fast IR spectroscopy monitors the photophysical or photochemical processes over time. Infrared bands with distinct absorbance frequencies (e.g. C=O stretching vibrations) allow transient species in metal carbonyl systems to be examined.  

As organometallic compounds include functional groups with characteristic frequencies, sensitive to molecular structure, this is a particularly useful tool for spectroscopic characterisation and kinetic studies. TRIR involves a pump and probe configuration where a laser pulse excites (“pumps”) a sample and IR spectroscopy operating in a very fast time range “probes” the generation of excited state transient species. Conventional ns TRIR systems use a XeCl excimer laser or Nd:YAG laser as the pump source, which operates at the 308 nm output of the XeCl excimer and the third harmonic (355 nm) of the Nd:YAG laser. A flow cell set up may be used during IR detection to avoid photodecomposition of the sample and allow for signal averaging. An IR probe source such as a globar (black body radiation) combined with a monochromator is frequently used, while for investigation of metal carbonyl photoreactions CO lasers have been utilized.  

Ultrafast TRIR systems such as the Picosecond Infrared Absorbance and Transient Excitation (PIRATE) facility at the Rutherford Appleton Laboratories (RAL) provide pump and probe spectroscopy with picosecond time resolution. This system allows the interrogation of the structural relaxation and reactivity of short lived (ps) intermediates formed in solution during a chemical reaction. A Ti:sapphire “pump” laser operating at 1KHz repetition rate with an average of 2 – 3 mJ per pulse is used while < 1 ps snap shots of the IR region of interest “probe” the progress of the reaction. TRIR studies discussed later were carried out at RAL and a full description of the TRIR spectroscopy instrumentation is available in a number of annual reports published by the Central Laser Facility at RAL.
1.7 Time correlated – single photon counting

Time correlated single photon counting (TC-SPC) is used to calculate luminescence lifetimes (or luminescence decay) by measuring the time of emission of individual fluorescent photons. The technique relies on the theory that the probability distribution for emission of a single photon after excitation yields the actual intensity against time distribution of all photons emitted as a result of the excitation. A probability distribution is constructed by measuring the single photon emission following a large number of excitation flashes. The time to amplitude convertor (TAC) is the essential part of the system as it transforms the arrival time of the photon between start and stop voltages. Simply put, it is not possible to measure the arrival time of all the photons emitted by the fluorescent species as a result of the excitation flash. Consequently arrival time of the first photon is recorded by the TAC and then only if it arrives in a given time interval after the flash.

A schematic diagram of the single photon counting instrumentation is shown in figure 14. Initially a flash of light excites a fluorescent species causing it to emit a photon from the excited state. Light from the excitation source is monitored by a photomultiplier (PM1) and a signal from it (the “start” signal) initiates the time sweep of the TAC. A second photomultiplier (PM2) monitors the fluorescent photons and the first photon registered by PM2 during the sweep of the TAC acts as a “stop” signal. An output signal is generated by the TAC, whose voltage is proportional to the time difference between the start and stop signals. This process is repeated to build up the time correlation. The pulse output of the TAC is amplified and used to sample a section of the time-to-amplitude convertor range. It is then expanded to cover the full range of a multichannel pulse height analyser (MCA). The MCA converts the voltage signal from the TAC to a time channel. Each channel is a unit division on the time axis and can be varied from 0.2 ns to a few microseconds per channel. The number of counts in each channel is directly proportional to the fluorescent intensity and so a probability histogram (counts versus time) is generated. The contents of the MCA are displayed on an oscilloscope where the build up of the fluorescence decay curve can be visually followed. The data collected consists of the sum of counts due to photon emission from the excited species and counts due to random background. Deconvolution methods are required to extract the inherent decay information. The quality
of the lifetime data is judged by two criteria: the random nature of the residual plot and the chi² (χ²) value which should be between 1 and 1.1.²⁷

Figure 14  Schematic diagram of single photon counting instrumentation.
1.8 Conclusions

The techniques discussed in this introductory chapter were applied to the compounds synthesised throughout this research. Thienylethynyl substituted porphyrins had their ground state and excited state properties investigated. The photophysics of a series of thienyl acetylenic compounds and their corresponding cobalt carbonyl complexes were examined. Pyridyl porphyrin metal carbynls (M = W or Cr) were examined by TRIR to elucidate the initial excited states populated following excitation. Finally the absorbance of a series of thienyl dipyrromethane dyes was obtained with a view to synthesising BODIPY complexes in the future. In all cases, assessment focused on the fundamental chemistry of the compounds in question in the hope that it shall enhance our ability to create and improve practical applications in photochemical processes.
1.9 Bibliography


Chapter 2

The synthesis, photophysics and electrochemical properties of a series of zinc(II) tetra thien-2-yl porphyrins and related zinc(II) tetra phenyl porphyrins.

Chapter two involves the study of thienyl porphyrins. This chapter begins with a literature survey on the synthesis, photophysics and electrochemistry of thienyl porphyrin systems. The synthesis of the porphyrins studied is given, followed by their photophysical and electrochemical properties. The effect of the thienyl moiety on the ground state and excited state properties of the porphyrin macrocycle is examined.
2.1 Literature Survey

2.1.1 Meso or β thienyl porphyrins (direct attachment to porphyrin macrocycle)

2.1.1.1 Synthesis

The first reported thienyl substituted porphyrin, meso tetra(thien-2-yl)porphyrin ($\text{H}_2\text{P1}$, Fig. 1) was synthesised by Triebs et al. in 1968. The direct condensation of pyrrole and 2-thiophenecarboxaldehyde via an adapted Rothemund method (route A, Fig. 1) resulted in the pure porphyrin in 9% yield. The Adler-Longo method, reacting equi-molar amounts of 2-thiophenecarboxaldehyde and pyrrole in refluxing propionic acid followed by recrystallisation, was later applied by Torrénas et al. however the yield was never reported (route B, Fig. 1). Both meso tetra(thien-2-yl)porphyrin and meso tetra(thien-3-yl)porphyrin, produced by the Adler-Longo method, using 2- and 3-thiophenecarboxaldehyde respectively to give the target compounds ($\text{H}_2\text{P1}$ and $\text{H}_2\text{P2}$, Fig. 2), was later reported by Bhyrappa and Bhavana.

![Figure 1] Rothemund (route A) and Adler-Longo (route B) synthesis of meso tetra(thien-2-yl)porphyrin ($\text{H}_2\text{P1}$).
Later the Lindsey method, the acid catalysed condensation of an aldehyde and pyrrole to form porphyrinogen followed by oxidation to give porphyrin, was applied to the synthesis of thienyl porphyrins. This method is advantageous as it avoids the highly oxidising environments of both the Rothenmund and Adler-Longo methods. Ono et al. synthesised a series of meso- and β- dodecasubstituted thienyl porphyrins (H₂P₁, H₂P₃, H₂P₄, H₂P₅, Fig. 2) including their zinc and copper metallated derivatives using an adapted version of Lindsey’s method. Thienyl carboxaldehydes and 3,4-diarylpyrroles were used to synthesise highly substituted dodecathienyl porphyrins in an attempt to alter the redox potentials of the macrocyclic structure by inducing ruffling of the planar geometry of the porphyrin.

![Lindsey Method](image)

**Figure 2** Synthesis and structures of highly substituted thienyl porphyrins reported by Ono et al.⁷
A series of uncrowded *meso* tetraarylporphyrins (e.g. $\text{H}_2\text{TPP}$) and β- octaarylporphyrins (e.g. 2,3,7,8,12,13,17,18-octaphenyl porphyrin) as well as a number of highly crowded systems including 5,10,15,20-tetrakis(thien-3-yl)-2,3,7,8,12,13,17,18-octaphenyl porphyrin ($\text{H}_2\text{P6}$, Fig. 3) and 5,10,15,20-tetraphenyl-2,3,7,8,12,13,17,18-octakis(thien-3-yl)-porphyrins ($\text{H}_2\text{P7}$, Fig. 3) were synthesised directly *via* the Lindsey method. Some intermediately crowded systems, such as nickel(II) 5,10,15,20-tetraphenyl-2,3-bis(thien-3-yl)porphyrin ($\text{NiP8}$, Fig. 3), were produced. The intermediately crowded porphyrin, $\text{NiP8}$, was synthesised by a Suzuki coupling reaction with nickel(II)-2,3-dibromotetraphenyl porphyrin and thiophene-3-boronic acid.

![Porphyrin structures](image)

**Figure 3** *Highly substituted porphyrins synthesised by Medforth et al.*

The majority of studies to date use an adapted Lindsey procedure as the milder conditions are better suited to thienyl porphyrin synthesis although a number of alternative approaches have been reported. Bonar-Law reported an innovative process towards porphyrin synthesis by producing a range of porphyrins in surfactant solution. This method involved multicomponent assembly in micelles. Micelles are dynamic clusters of surfactant molecules which have the ability to collect and concentrate species from aqueous solution and so promote porphyrinogen assembly by binding the product more tightly than the reactants. The initial steps of the reaction are: the concentration of the reactants in the micelle, their condensation into linear chains and their cyclisation into porphyrinogen.
Subsequently, the porphyrinogen is irreversibly oxidised to the porphyrin. Several aspects of this method were investigated including the time course of the reaction, reactant and surfactant concentration, as well as the reversibility of the reaction. In this way freebase *meso* tetra(thien-2-yl)porphyrin (H$_2$P1, Fig. 2) was produced, with an isolated yield of 24 %, which is comparable to reported yields via the Lindsey procedure.

Most recently, a novel high yielding synthesis of *meso* substituted porphyrins has been reported by Shi and Wheelhouse. Using an adapted method of Lindsey and Woodfords, commercially available porphine was initially converted to Mg(II)-porphine. Mg(II)-5,10,15,20-tetrakisbromoporphine was synthesised via bromination of the Mg(II)-porphine precursor in 81 % yield. Using standard Suzuki conditions, the authors coupled aryl boronic acid groups to the porphyrin macrocycle and afterwards removed the magnesium ion to yield the desired freebase porphyrins (Scheme 1). In this manner freebase tetra(thien-3-yl)porphyrin (H$_2$P2, Fig. 2) was produced in 41 % total yield, the highest yield reported to date. However as former methods involve the yield limiting porphyrinogen cyclisation step this method cannot be directly compared as the yield is based purely on the functionalisation of the commercially sourced porphine.
The Mac Donald 2+2 procedure,\textsuperscript{12} involving the condensation of 3-formylthiophene with dipyrromethane to synthesise a \textit{trans} porphyrin, 5,15-bis(thien-3-yl)porphyrin (H$_2$P$_9$, Fig. 4), was reported by Arminger and Lash.\textsuperscript{13} The thien-2-yl isomer, 5,15-bis(thien-2-yl)porphyrin (H$_2$P$_{10}$, Fig. 4), was later synthesised by a similar method.\textsuperscript{14}
Similarly, the condensation of an alkylated dipyrrromethane and 2-thiophenecarboxaldehyde in the presence of trichloroacetic acid with subsequent oxidation of the porphyrinogen resulted in the formation of $\text{H}_2\text{P}11$ (Fig. 5). The reaction of the dipyrrromethane with 2’,5-bithienylcarboxaldehyde gave $\text{H}_2\text{P}12$ (Fig. 5). Their metal complexes ($\text{ZnP}11$, $\text{ZnP}12$, $\text{CuP}11$ and $\text{CuP}12$) were readily produced using metal acetates.
A series of *trans* porphyrins have been synthesised by Collis and co-workers using an adapted Lindsey method.\textsuperscript{16} Alkylated dipyrrromethanes were condensed with 2-/3-thiophenecarboxaldehyde to produce 5,15-bis(thienyl)porphyrins (H\textsubscript{2}P\textsubscript{13}, H\textsubscript{3}P\textsubscript{14}, H\textsubscript{3}P\textsubscript{15}, H\textsubscript{2}P\textsubscript{16} Fig. 6) with isolated yields of between 16 and 65\%. Further treatment of H\textsubscript{2}P\textsubscript{14} with zinc acetate produced the metallated derivative (ZnP\textsubscript{14}).

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{porphyrin Structures.pdf}
\caption{Examples of *trans* substituted porphyrins.\textsuperscript{16}}
\end{figure}

The sterically hindered porphyrin *meso* tetrakis-5,10,15,20-([2’,2’’:5”,2”’-terthiophen]-3”-yl)porphyrin, (H\textsubscript{2}P\textsubscript{17}, Fig. 7), and its *trans* substituted homologue, 5,15-bis([2’,2’’:5”,2”’-terthiophen]-3”-yl)-2,8,12,18-tetra-\textit{n}-butyl-3,7,13,17-tetramethyl porphyrin (H\textsubscript{3}P\textsubscript{18}, Fig. 7), were produced under Lindsey conditions from 3-formylthiophene. Initially H\textsubscript{2}P\textsubscript{17} was synthesised using trifluoroacetic acid as catalyst with a resulting yield of 17\%. Repeating the procedure but using boron trifluoride diethyl etherate as the Lewis acid catalyst, resulted in a significantly higher yield (34\%) of the porphyrin. However \textsuperscript{1}H NMR analysis revealed a complex array of signals. Due to the bulky nature of the terthiophene moiety, the product contained a mixture of four inseparable atropisomers. Molecular modelling indicated that the β-pyrrolic hydrogen clearly prevented the rotation of the bond joining the central thiophene ring, due to its interaction with the outer thiophene rings of the terthiophene moiety. Complete metallation of the porphyrin mixture proved difficult, due to the steric constraints imposed by some of the atropisomers. Condensation of 3’-
formylterthiophene with dipyrromethane gave the \textit{trans} porphyrin $\text{H}_2\text{P18}$ as a mixture of $\beta\beta$- and $\alpha\beta$- atropisomers. $^1$H NMR of the product indicated a statistical mixture of the $\beta\beta$-\textit{trans} and $\alpha\beta$-\textit{trans} porphyrin.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure7}
\caption{\textbf{P17 and P18} terthienyl porphyrins.}
\end{figure}

Novel mono-substituted thienyl porphyrins zinc(II)-5-(5’-carboxythien-2’-yl)-10,15,20-trimesitylporphyrin (\textit{ZnP19}, Fig. 8) and zinc(II)-5-(4’-carboxythien-2-yl)-10,15,20-trimesitylporphyrin (\textit{ZnP20}, Fig. 8) have also been reported.\textsuperscript{17} The precursor to $\text{H}_2\text{P19}$, 5-(5-methoxycarboxylthien-2-yl)-10,15,20-trimesitylporphyrin was synthesised \textit{via} the Lindsey method and then hydrolysed to yield the target freebase porphyrin. Subsequent
metallation gave ZnP19. 5-(4’-cyanothien-2-yl)-10,15,20-trimesitylporphyrin, also produced by the Lindsey method, was converted to H2P20 and then to the zinc analogue ZnP20.

![P19 and P20](image)

**Figure 8** Mono-substituted carboxythienylporphyrins.

Utilising C-C coupling reactions thienylporphyrins can be further functionalised. Rochford et al. synthesised a complete series of mono-, di-, tri- and tetra- meso (thien-2-yl)porphyrins (H2P21 – H2P26, Fig. 9) to fully investigate the influence of the thiophene ring on the ground and excited state properties of meso porphyrins. The tetra substituted porphyrins were prepared according to Lindsey’s standard procedure. The mono-, di- and tri- substituted porphyrins were prepared by a mixed aldehyde condensation of 5-bromo-2-thiophenecarboxaldehyde, benzaldehyde and pyrrole followed by metallation with zinc acetate and Sonogashira coupling with trimethylsilylacetylene. *Meso* trithienyl and triphenyl-porphyrin-ferrocene dyads (H2P27 and H2P28, Fig. 37) were similarly synthesised via Lindsey’s mixed aldehyde condensation and converted to their zinc(II) analogues. The ground and excited state properties were then examined and compared to ZnP1.
Figure 9 Various thienyl porphyrins with extended conjugation.

Modern metal-catalysed bond-forming reactions were employed and facilitated the construction of ZnP29 – ZnP34 (Fig. 10).\textsuperscript{20a} Combining electron-rich Suzuki-porphyrin synthon precursors, a variety of appropriately functionalised porphyrins were produced. These chromophores possess electron-poor thiophene and oligothiophene species linked by a direct carbon-carbon single bond or conjugated through an intervening ethynyl unit. Following this work, a series of conjugated zinc(II) porphyrin-based chromophores related to ZnP32 were synthesised (ZnP35 – ZnP38, Fig. 11) via similar metal catalyzed cross-coupling reactions.\textsuperscript{20b}
Figure 10  \( \text{ZnP29} - \text{ZnP38} \)
Efficient intramolecular energy transfer from an anthryl donor moiety to a porphyrin acceptor via terminally substituted oligothiophene bridging units was reported for a large series of compounds (H$_2$P39 – H$_2$P59, Fig. 11 and Table 1). The porphyrins were synthesised via Lindsey’s method with a mixed aldehyde reaction, where yields were consistent with a statistical incorporation of two aldehydes (6 – 10 %). n-Pentyl groups were incorporated into the oligothiophene chain to increase their solubility.

![Diagram of R groups used to make porphyrin-oligothiophene-anthracene triads.](image)

*Figure 11*  R groups used to make porphyrin-oligothiophene-anthracene triads.
Table 1  
\textbf{R groups used to make porphyrin-oligothiophene-anthracene triads.}

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Post functionalisation of the porphyrin ring is often carried out in the preparation of polymeric thiényl systems. \textit{Meso} tetrakis(2’5-bithienyl)porphyrin \(\text{H}_2\text{P60}\) (Fig. 12) and \textit{meso} tetrakis([5’,2”’:5’’’,2’’’'-terthiophen]-2’-yl) porphyrin \(\text{H}_2\text{P61}\) (Fig. 12) were produced from the corresponding oligothiénylcarboxaldehydes under standard Adler-Longo conditions, and their zinc(II) and palladium(II) metallated analogues were subsequently synthesised.\textsuperscript{22} Two-dimensional porphyrin polymers containing oligothiényl bridges in the lateral direction were prepared by electrochemical oxidation of the \textit{meso} tetrakis(oligothiényl)porphyrin metal complexes (Fig. 24).
The crystal structure of **ZnP1** (Fig. 2) indicates that the porphyrin possesses a wave like conformation with the central zinc ion residing in an inversion centre.\textsuperscript{23} The macrocycle has a four coordinate geometry and a 24 atom core similar to zinc tetraphenylporphyrin (**ZnTPP**). **CuP1** (Fig. 2) was found to have a near planar porphyrin core with only slight puckering with a deviation of less than 0.01 Å observed for individual atoms in the mean plane.\textsuperscript{24} In contrast **ZnP2** (Fig. 2) exhibits unusual planar and non-planar core features (Fig. 13).\textsuperscript{25} In the case of the planar core, only minimal deviation from planarity is observed with the β-pyrrolic carbons showing marginal deviation from the mean plane (± 0.034 Å). In the case of the non-planar thienyl porphyrin, the β-pyrrolic carbons show significant deviation (± 0.422 Å) over the mean plane. This deviation suggests the conformation is a combination of saddle and marginal ruffle.
Figure 13  Solid state crystal structure of the planar unit of ZnP2, (i) and (ii) indicate the side view of the planar and non-planar porphyrin units respectively.25

The crystal structure of 5,10,15,20-tetrakis(5-methylthien-2-yl)porphyrin, H₂P62, possesses an essentially planar geometry with a slight waving conformation.26 A direct correlation between the degree of porphyrin distortion and the bathochromic shift in the absorbance spectra was shown for a series of meso-, β- overcrowded porphyrins.7 The macrocyclic core of the trans porphyrin (H₂P10, Fig. 4) adopts a saddle like conformation in the solid state with the two meso thienyl arms parallel to each other.14 These arms are tilted with respect to the porphyrin mean plane at angles of ~ 50° (smaller than that of ZnP2). The porphyrins formed parallel layers aligned through the aromatic core with thienyl groups forming a staggered arrangement. The aromatic core of the porphyrins formed a supramolecular columnar structure (Fig. 14).
Figure 14  Side view of stacking arrangement generated by $\text{H}_2\text{P10}$ in the solid state.$^{14}$
2.1.1.2 Electronic and photophysical properties

The electronic and photophysical properties of thienyl porphyrins were investigated by several groups though there has been little consistency in describing the influence of the thienyl ring on the electronic properties of the porphyrin macrocycle. The absorbance spectrum of thienyl porphyrins has long been known to shift to longer wavelengths when compared to the tetraphenylporphyrin analogues. The spectral profile of the zinc(II) and copper(II) metallo derivatives (ZnP1, ZnP2, CuP1, CuP2, Fig. 2) reported by Bhyrappa and Bhavana are quite similar to those of the corresponding tetraphenylporphyrin (ZnTPP and CuTPP), each displaying an intense Soret and two Q bands. Some minor bathochromic shifts were observed for ZnP1 (ZnTPP: 422 nm, ZnP1: 427 nm, ZnP2: 422 nm), as shown in figure 15 with greater shifts observed for the copper analogues (CuTPP: 415 nm, CuP1: 421 nm, CuP2: 418 nm). The molar extinction coefficients were found to be comparable to other porphyrins.

![Electronic absorbance spectra of ZnTPP (blue line) and ZnP1(red line) in CH2Cl2.](Image)

*Figure 15* Electronic absorbance spectra of ZnTPP (blue line) and ZnP1(red line) in CH2Cl2.
Sun et al. reported the absorbance $\lambda_{\text{max}}$ and extinction coefficients of $\text{H}_2\text{P1}$, $\text{H}_2\text{P63}$, $\text{H}_2\text{P64}$, $\text{H}_2\text{P65}$ (Fig. 16) and observed red shifts of between 10 - 15 nm with respect to $\text{H}_2\text{TPP}$.

They postulated that the spectral shifts in the UV-vis spectra were due to an inductive effect by the thienyl group as opposed to the increased conjugation of the porphyrin $\pi$ – system.

![Substituted meso thienyl porphyrins $\text{H}_2\text{P63} – \text{H}_2\text{P65}$](image)

More recently Brückner et al. investigated the electronic absorbance properties of a series of thienyl porphyrins ($\text{H}_2\text{P1}$ and $\text{H}_2\text{P2}$, Fig. 2, $\text{H}_2\text{P63}$ and $\text{H}_2\text{P64}$, Fig. 17). The Soret and Q bands of all the thienyl porphyrins were red shifted to some extent when compared to $\text{H}_2\text{TPP}$ with its Soret band at 417 nm (Table 2). A bathochromic shift of 9 nm to 426 nm was reported for $\text{H}_2\text{P1}$ with respect to $\text{H}_2\text{TPP}$. The Soret band of $\text{H}_2\text{P2}$ was only slightly shifted to 421 nm (+ 4 nm). However the Soret band of methyl substituted thien-2-yl porphyrins was red shifted by some 8 – 13 nm depending on the position of the methyl group. Methyl substitution at the 5’ position as in $\text{H}_2\text{P63}$ resulted in a further 4 nm bathochromic shift to 430 nm, whereas substitution at the 3’ position in $\text{H}_2\text{P64}$ gave a slight hypsochromic shift (-1 nm to 425 nm). These observations although not conclusive do indicate the direct influence of the meso thienyl substituents on the electronic properties of the central porphine ring.
<table>
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<th>Porphyrin</th>
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<th>( \lambda_{\text{em}} ) (nm)</th>
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<td>514, 549, 588, 647</td>
<td>651, 715</td>
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<td>670, 720 (sh)</td>
<td>9</td>
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<td>519, 556, 594, 653</td>
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<td>8</td>
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<td>526, 569, 597, 665</td>
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<td>9</td>
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<tr>
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<td>520, 557, 597, 660</td>
<td>666, 725</td>
<td>6</td>
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</table>

**Table 2**  
*Absorbance and emission data of meso tetrathienylporphyrins and \( \text{H}_2\text{TPP} \) in \( \text{CH}_2\text{Cl}_2 \).* \(^{28}\)

As part of the investigation into the origin of these bathochromic shifts in the absorbance spectra of thienyl porphyrins, density functional theory was employed by Brückner et al. to compute the energy of the porphyrin system as a function of the rotation of a single meso aryl group. \(^{28}\) There is less steric hindrance for the smaller 5 membered *meso* thienyl ring than for the larger 6 membered phenyl ring. In addition the thien-2-yl group lacks one ortho-phenyl H to \( \beta \)-pyrrole H interaction (Fig. 18). This should allow greater ease of rotation for the thien-2-yl porphyrins and also a somewhat more facile rotation for the thien-3-yl porphyrins. The computed rotational barriers of \( \text{H}_2\text{P1} \) and \( \text{H}_2\text{P2} \) confirm this greater ease of aryl rotation, being 50 and 75 % lower than that of \( \text{H}_2\text{TPP} \) respectively.

This suggests that, the previous proposal, of bathochromic shifts observed in thienyl porphyrins, due to the thienyl rings inductive effect, is over simplified. The molecular modelling results indicate that these shifts may be more dependent on the conformation which the thienyl groups adopt, allowing \( \pi-\pi \) orbital overlap of the thienyl and porphyrin ring systems, as opposed to solely the thienyl inductive effect.
A direct correlation between the degree of porphyrin distortion and the bathochromic shift in absorbance spectra was shown for the overcrowded porphyrins ($H_2P3$, $H_2P4$, $H_2P5$, Fig. 2). Remarkable bathochromic shifts of up to 100 nm of the Soret bands were observed. $H_2P3$ and $H_2P5$ have Soret bands with $\lambda_{\text{max}}$ at 508 and 520 nm respectively. The Soret band of 2,3,5,7,8,10,12,13,15,17,18,20-dodecaphenylporphyrin was observed at 466 nm, indicating that along with the distortion of the macrocycle there is another factor influencing the bathochromic shifts in thienyl porphyrins.

A more recent study on porphyrins $ZnP21$ – $ZnP26$ (Fig. 9) suggests that the direct attachment of the aromatic thiophene ring at the meso position of the porphyrin ring does lead to electronic interaction of the two $\pi$-systems which can be enhanced by appropriate substitution. By varying the substituent on the thiophene ring a bathochromic shift can be observed in the Soret band of the porphyrin. Again, when compared to $ZnTPP$ the Soret band of $ZnP1$ was red shifted by 8 nm to 430 nm, while the other tetra substituted porphyrins $ZnP21$, $ZnP22$ and $ZnP23$ are shifted by an additional 4 nm, 8 nm and 6 nm respectively. Such a strong shift would not be predicted on the basis of an inductive effect alone. More likely is the increased coupling of the overlapping $\pi$ systems of the porphyrin and thiophene rings as is evidenced in the increasing FWHM of the porphyrin Soret.
Varying the number of 5-trimethylsilylethynylthien-2-yl groups around the porphyrin (ZnP24, ZnP25 and ZnP26) also induces a 4 nm bathochromic shift for each thienyl moiety added (when compared to ZnTPP $\lambda_{\text{max}} = 422$ nm) such that the Soret band of ZnP26 is observed at 438 nm.

The fluorescence spectrum of thienyl porphyrins exhibit characteristic singlet state emission consisting of two vibronic bands i.e. $Q(0,0)^*$ and $Q(1,0)^*$ in the range 550 - 800 nm (Fig. 19).\textsuperscript{18} In the fluorescence spectrum of $\text{H}_2\text{TPP}$ two $\lambda_{\text{max}}$ are observed at 652 and 716 nm corresponding to $Q(0,0)^*$ and $Q(1,0)^*$. $\text{H}_2\text{P2}$ exhibits red shifted bands at 658 and 723 nm and even more bathochromically shifted is the spectrum of $\text{H}_2\text{P1}$ with bands at 666 and 722 nm.\textsuperscript{25} Fluorescence quantum yield ($\Phi_{fl}$) of 0.006 was reported for $\text{H}_2\text{P1}$. This is lower than the values reported for $\text{H}_2\text{P2}$ (0.010) and $\text{H}_2\text{TPP}$ (0.120). A similar trend was observed for the zinc metallated derivatives with ZnP1 and ZnP2 exhibiting emission bands at 618, 658 and 605, 653 nm respectively. The fluorescence quantum yields of the metal complexes (ZnP1: 0.0013, ZnP2: 0.004) are also reduced compared to ZnTPP (0.033). The decrease in quantum yield of thien-2-yl porphyrins relative to thien-3-yl porphyrins has been attributed to the closer proximity of the sulphur to the porphyrin $\pi$-system.\textsuperscript{25}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure19.png}
\caption{Steady-state emission spectrum of ZnTPP (blue line) and ZnP1 (red line) recorded in CH$_2$Cl$_2$ at room temperature.}
\end{figure}
A reduction in singlet state lifetime was observed for the thienyl porphyrins (H$_2$P1, Fig. 2 and H$_2$P63, H$_2$P64, H$_2$P65 Fig. 20) with respect to H$_2$TPP (Table 3). This is attributed to the presence of the four “heavy” sulphur atoms on the periphery of the macrocycle. However, suggestion of π-π overlap of the thienyl and porphyrin systems was also implied by the authors.

<table>
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<th>Porphyrin</th>
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<th>$k_f$ (1 / ns)</th>
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Table 3  Luminescence data of thien-2-yl porphyrins and H$_2$TPP in toluene at ambient temperature.\(^{27}\)

![Fluorescence decay signals](image)

Figure 20  Fluorescence decay signals of H$_2$TPP, H$_2$P1 (1), H$_2$P62 (3), H$_2$P63 (2) and H$_2$P64 (4) in toluene at ambient temperature. The detection wavelength is 660 nm. IRF indicates the instrument response function.\(^{27}\)
The fluorescence lifetimes of zinc(II) thienylporphyrins ZnP21 – ZnP26 (Fig. 9) are in the range 1.36 – 0.52 ns. The shortest lifetime was that of ZnP21, bearing four heavy bromine atoms and it also possessed the lowest fluorescence quantum yield. The fluorescence emission spectra of ZnP24 – ZnP26 show increased intensity with a concurrent red shift of their λ_{max} as the number of 5-trimethylsilylethynylthien-2-yl moieties were added, when compared to ZnTPP. The fluorescence quantum yield (Φ_{fl}) of the mono- and di-(5-trimethylsilylethynylthien-2-yl)porphyrins increase by 39 % and 27 % respectively compared to ZnTPP. Triplet excited state \( ^3(\pi-\pi^*) \) absorbance spectra and transient absorbance lifetimes were also obtained. Similar to ZnTPP, each porphyrin displayed a weak absorbance in the UV region with another more intense absorbance in the visible in the region. In the case of ZnTPP the λ_{max} is observed at 470 nm, however with the meso tetra(thien-2-yl)porphyrins the λ_{max} of each is observed in the region between 490 – 500 nm. A substantial increase in absorbance was also observed in the region 580 – 780 nm which the authors attribute to charge transfer to the peripheral thein-2-yl π system. ZnP24, ZnP25, ZnP26 and ZnP22 are all red shifted relative to ZnTPP with their λ_{max} occurring at 480, 480, 490 and 500 nm respectively. A decrease in triplet lifetime is observed for ZnP1 (20 µs) ZnP21 (7 µs) ZnP22 (12 µs) and ZnP23 (13 µs) relative to ZnTPP (24 µs). Increasing the number of 5-trimethylsilylethynylthien-2-yl moieties on the porphine also resulted in a decrease in the triplet lifetime: ZnP24 (16 µs), ZnP25 (11 µs) and ZnP26 (10 µs). These excited state characteristics suggest relatively strong coupling of the porphyrin ring and the thien-2-yl π framework upon excitation. The combined studies of Brückner et al. and Rochford et al. show considerable electronic communication between the thienyl and porphyrin π-systems in both the ground and excited states. Thus earlier studies on thienyl porphyrins implying inductive effects alone were responsible for the change in photophysical properties relative to phenyl porphyrins need to be revised.

In trans thienyl porphyrins, the classic electronic spectra of the porphyrin is retained although it is hypsochromically shifted compared to both H₂P1 (Fig. 1) and H₂TPP. The unsubstituted trans thienylporphyrin (H₂P10, Fig. 4) presents an intense Soret band with a maximum absorbance at 411 nm, with the Q bands showing a similar blue shift. The emission spectrum of H₂P10 possesses a strong fluorescence, centred at 642 nm with a weak shoulder at 707 nm. The emission pattern is very similar to that of H₂TPP (λ_{em} =
653, 721 nm) only slightly blue shifted. The photophysical properties of the mono substituted porphyrins (Fig. 8) were also examined.\textsuperscript{17} The Soret band at 425 nm for ZnP19 and 424 nm for ZnP20 are very similar to those of ZnP1 ($\lambda_{\text{max}} = 426$ nm) but appear broader. The slightly increased broadening in ZnP19 compared to ZnP20 may be caused by the larger conjugation between the porphyrin core and the thiophene in ZnP19. The emission of ZnP19 and ZnP20 occurs at 608, 660 nm and 606, 661 nm respectively.

The on/off switching of porphyrin fluorescence through the use of a ferrocene/ferricenium (Fc/Fc\textsuperscript{+}) redox couple was reported for the zinc(II) tri(thien-2-yl)porphyrin-ferrocene dyad, ZnP27 (Fig. 37).\textsuperscript{19} The $^1(\pi-\pi^*)$ fluorescence of ZnP27 is almost completely quenched in comparison to both ZnP1 (Fig. 2) and ZnTPP, with no evidence of the $^3(\pi-\pi^*)$ excited state observed by transient absorbance spectroscopy (Fig. 21). Attachment of the ferrocene substituent at the meso position quenched both the $^1\pi-\pi^*$ and $^3\pi-\pi^*$ excited states of the porphyrin ring by a rapid electron transfer mechanism. The fluorescence of the dyad can be “switched on” by oxidation of the ferrocene to the ferricenium ion. The Fc/Fc\textsuperscript{+} redox couple occurs 40 mV positive of the unsubstituted ferrocene and results in the appearance of a low-energy ferricenium ligand-to-metal charge transfer absorbance at 767 nm. Oxidation of Fe(II) to Fe(III) restores the porphyrin emission through preclusion of the electron-transfer process. The relative fluorescence quantum yield for ZnP27\textsuperscript{+} is 71 % with respect to ZnP1 the minor decrease in fluorescence is attributed to the quenching processes of intersystem crossing of the porphyrin $^1(\pi-\pi^*)$ excited state to the new LMCT state and energy transfer quenching by the ferricenium unit. Transient absorbance spectroscopy of the ZnP27\textsuperscript{+} dyad produced transient signals indicative of the $^3(\pi-\pi^*)$ triplet excited state (Fig. 21). A triplet lifetime of 20 $\mu$s was obtained for ZnP27\textsuperscript{+}, a reduction of 50 % in comparison to ZnP1 (40 $\mu$s). Similarly, the $^1(\pi-\pi^*)$ singlet excited state lifetime of 0.31 ns observed for ZnP27\textsuperscript{+}, is shorter than that of ZnP1 (0.56 ns).
The electronic absorbance properties of porphyrins, ZnP29 – ZnP34 (Fig. 10), were examined (Table 4) and results indicated that both the $\lambda_{\text{max}}$ of the Q bands and emission spectra are primarily dependent on whether the thiophene unit was linked to the macrocycle directly at the meso-carbon position (ZnP29 – ZnP31) or through an intervening ethynyl unit (ZnP32 – ZnP34) and was also affected by the number of thiophene units (n = 1, 2 or 3). Modest Stokes shifts (350 to 1300 cm$^{-1}$) indicate that the derivatised zinc(II)porphyrins undergo modest to substantial excited state structural distributions. For each mode of connectivity the porphyrins that possess only a single thiophene unit (ZnP29 and ZnP32) display the largest Stokes shift within their respective class. Consistent with this, ZnP29 and ZnP32 exhibit emission maxima at 698 nm and 714 nm the lowest energy within their respective structural class. The emission maxima of each class also follow a similar trend, in that; they shift hypsochromically with increasing number of thiophene units. The porphyrins with thiophene units bonded directly at the meso position (ZnP29 – ZnP31) displayed emission maxima values at 698, 669 and 662 nm respectively while porphyrins linked to the thiophene through the ethynyl moiety
(ZnP32 - ZnP34) displayed bathochromically shifted emission maxima which shift hypsochromically with increasing number of thiophene units at 714, 706 and 700 nm respectively. This is indicative of the increased excited-state electronic dipole moment due to extensive porphyrin-thiophene conjugation. ZnP35’s formyl group caused a blue shift in the Q band $\lambda_{\text{max}}$ (676 nm), whereas the strong dicyanovinyl acceptor group in ZnP36 caused a red shift ($\lambda_{\text{max}} = 698$ nm) relative to ZnP32 ($\lambda_{\text{max}} = 685$ nm).

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<th>$\lambda_{\text{em}}$ (nm)</th>
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Table 4  
**Electronic data of ZnP29 – ZnP38 recorded in THF.**

In spite of the direct attachment of the $\pi$-systems of anthracene, oligothiophene and porphyrin in H$_2$P39 – H$_2$P59 (Fig. 11), the individual molecular subunits were observed in the UV-vis spectra as in the spectra of supramolecular systems (Table 5). For all anthracene-oligothiophene-porphyrin molecules, highly selective excitation of the terminal 9-anthryl unit at 258 nm is possible. The supramolecules all possess typical singlet emission from the porphyrin Q(0,0)* and Q(1,0)* emission bands. The emission bands are broadened and red shifted (~7 nm) compared to H$_2$TPP. Upon excitation at 258 nm, both
H$_2$P$_{46}$ and H$_2$P$_{49}$ possess the typical porphyrin emission indicating energy transfer from the anthracene to the porphyrin chromophore. The authors estimate, on the basis of perfect matching of absorbance and excitation spectra, that energy transfer efficiency is 98%. The bithiophene bridged systems, H$_2$P$_{42}$ and H$_2$P$_{44}$, gave analogous results. Thus singlet-singlet energy transfer is the only quenching process involved. Similar results were found on increasing the length of the oligothiophene chain in H$_2$P$_{55}$ - H$_2$P$_{59}$. Excitation of the intensive anthracene transition led to typical emission from the porphyrin end group. The mechanism of energy transfer, i.e. Förster or Dexter, could not be clearly defined for these systems. The authors did suggest however that due to vibronic coupling, energy is transferred from the anthryl donor to the porphyrin acceptor via an intramolecular vibrational relaxation process mediated by the oligothiophene chain. On comparing these results with similar polyene based systems Würthner et al. concluded that oligothiophenes were far superior with regard to mediating energy transfer and showed greater potential for application in molecular electronics.

<table>
<thead>
<tr>
<th>Porphyrin</th>
<th>Anthracene $\lambda_{\text{max}}$ (nm)</th>
<th>Soret band $\lambda_{\text{max}}$ (nm)</th>
<th>Q bands (nm)</th>
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<td>H$<em>2$P$</em>{41}$</td>
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<td>421</td>
<td>522, 559, 600, 657</td>
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<tr>
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<td>426</td>
<td>524, 564, 599, 657</td>
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<tr>
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<td>258</td>
<td>422</td>
<td>522, 559, 599, 657</td>
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<tr>
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<td>258</td>
<td>428</td>
<td>525, 565, 600, 659</td>
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<tr>
<td>H$<em>2$P$</em>{49}$</td>
<td>258</td>
<td>435</td>
<td>526, 573, 598, 663</td>
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<tr>
<td>H$<em>2$P$</em>{55}$</td>
<td>254</td>
<td>419</td>
<td>519, 555, 601, 659</td>
</tr>
</tbody>
</table>

Table 5 Absorbance data for some of the supramolecular systems recorded in n-hexane.$^{21}$

Okada et al. investigated substituent control of J-aggregate formation of insoluble porphyrins in protonated water.$^{29}$ Working primarily with phenyl substituted porphyrins it was found that substituents at the meso position affected aggregation to a higher extent.
Porphine and octaethylporphyrin did not form \textit{J}-aggregates, indicating that aromatic rings at the \textit{meso} position are necessary for aggregate formation. Furthermore aromatic rings with large steric bulk also did not aggregate. In protonated solution, however \textit{H}_{3}\textit{P}_{2} (Fig. 2) did form \textit{J}-aggregates. This was evidenced by changes in the absorbance spectra. The Soret band of the freebase monomer (420 nm) is first replaced by the protonated monomer absorbance (447 nm) which is in turn exchanged by a new absorbance at 481 nm. Simultaneously the observed Q band at 652 nm is bathochromically shifted to 678 nm and subsequently 756 nm. These bathochromic shifts in the absorbance spectra signify the assembly of “head-to-tail” aggregates. In most cases, AFM images of the \textit{J}-aggregate films revealed square rod like microcrystals. The Soret band remained around 480 nm for the aggregates however the Q band absorbances were found to vary widely from 658 to 756 nm. It was also noted that the electron-donating character of the \textit{meso} substituents affected the FWHM of the Q bands. These changes in the absorbance spectra suggest that the energy levels of the excited states of the porphyrin \textit{J}-aggregates are substituent dependant.
2.1.1.3 Electrochemical properties and electropolymerisation

By monitoring shifts in the anodic and cathodic redox processes of the porphyrin the influence of the thienyl group on the HOMO and LUMO energies can be further examined. Each of the thienyl porphyrins, H$_2$P1, H$_2$P2 and their zinc and copper analogues (Fig. 2), displayed two successive one-electron oxidations and two successive one-electron reductions (Fig. 22).

H$_2$TPP was also examined to delineate the effect of the thienyl groups. The observed potentials revealed striking differences in oxidation and reduction of H$_2$P1 relative to H$_2$P2 and H$_2$TPP. Both thienyl porphyrins showed a cathodic shift of the first oxidation (50 mV for H$_2$P1$^{+/0}$ and 110 mV for H$_2$P2$^{+/0}$) with respect to H$_2$TPP (+1.0 V vs. Ag/AgCl). The first reduction of H$_2$P2 was within experimental error when compared to H$_2$TPP, however H$_2$P1$^{0/-}$ showed a substantial anodic shift of 140 mV which was primarily responsible for its reduced band gap and lower energy absorbance. A HOMO-LUMO energy gap of 1.98 eV was calculated for H$_2$P1 compared to 2.18 eV for to H$_2$P2 and 2.23 eV for H$_2$TPP. Similar trends were observed for the metallated analogues with the redox potentials of ZnP2 and CuP2 approaching those of ZnTPP and CuTPP.

While the authors ascribed this band gap narrowing to thienyl substitution inductive effects the results can similarly be explained by the $\pi$-$\pi$ overlap of the porphyrin and thienyl structures resulting in stabilisation of both the HOMO and LUMO orbitals, which corresponds well with the ground and excited state trends observed by Brückner et al. and Rochford et al. The electrochemical properties of H$_2$P1 (Fig. 2), H$_2$P62, H$_2$P63 and H$_2$P64 (Fig. 12) were also investigated by cyclic voltammetry. However in contrast to the previous results, the latter study showed two one-electron oxidations and only one, one-electron reduction process.
Substitution of the thien-2-yl moiety caused significant changes in the redox potentials as observed in the cyclic voltammetry studies of ZnP21 – ZnP26 (Fig. 9). All porphyrins showed two one-electron oxidations and two one-electron reductions. The meso tetra(thien-2-yl)porphyrins showed an anodic shift in their first oxidation (ZnP1+/0 0.43, ZnP21+/0 0.61, ZnP24+/0 0.49, ZnP23+/0 0.49 V vs. Fc/Fc+) when compared to ZnTPP+/0 (0.34 V vs. Fc/Fc+), indicating stabilisation of the HOMO orbital of the porphyrin ring system. Stabilisation of the LUMO orbitals also occurred with a decrease in the potential of the first reduction. Again ZnP21 showed the largest effect with a decrease in its reduction potential of 240 mV compared to ZnTPP0/-1.85 V vs. Fc/Fc+. Increasing stabilisation of the HOMO and LUMO was observed on increasing thienyl substituents on the porphyrin ring as seen in ZnP24, ZnP25, ZnP26 and ZnP22. A decrease in the reduction potential (i.e. LUMO energy) appeared to be the dominant factor in reducing the calculated HOMO-LUMO energy gap for these systems. The reduction in the band gap follows the order ZnP22 (2.02 eV), ZnP26 (2.02 eV), ZnP25 (2.04 eV), ZnP24 (2.06 eV) and ZnTPP (2.09 eV). Therefore by controlling the number of thienyl substituents on the porphyrin as well as the nature of the thienyl ring itself the band gap may be manipulated.
It is well established that the HOMO orbital of the porphyrin macrocycle is destabilised upon reduction of its planarity. Puckered porphyrins are easier to oxidise where as reduction is insensitive to the distortion, which lowers the HOMO-LUMO energy gap. This was realised in the redox properties of the copper(II) metallated derivatives of the highly substituted porphyrins, CuP3, CuP4 and CuP5, along with CuP1 (Fig. 2). Substitution of the porphyrin ring with thien-2-yl moieties in the meso- and β-positions increased the energy of the HOMO orbital as expected, however a stabilisation of the LUMO orbital also occurred resulting in an overall decreased energy gap of 1.89 eV for CuP4, 1.63 eV for CuP3 and 1.48 eV for CuP5. HOMO-LUMO energy gaps of 2.34 eV and 2.20 eV were reported for CuTPP and CuP1.

Two reversible waves occur at -1.58 V and -2.04 V vs. SCE for trans dithienylporphyrin (H2P10, Fig. 4). Continual sweeps of H2P10 resulted in the deposition of a thin insoluble polymer on the electrode. Further investigation of this polymer layer showed that it belongs to the restricted family of “zero bandgap” polymers, that is, the oxidation potential is less than or equal to its reduction potential. Porphyrins with band gaps as low as +0.8 and +0.35 eV vs. SCE (H2TPP and ZnTPP respectively) have been previously reported. This is the first “zero bandgap polymer” in a poly (aryl-porphyrin) series. The authors are continuing their studies in order to explain such electrochemical behaviour.

Polymerisation by electrochemical oxidation was carried out on trans dithienylporphyrins ZnP11 and CuP11 (Fig. 5). Following electrochemical oxidation, the zinc(II) and copper(II) polymers, poly-ZnP11 and poly-CuP11, were deposited on the surface of a gold-plate electrode. Peak currents at +1.1 V and +0.9 V vs. SCE, attributed to coupling of the thienyl groups at the meso position of the porphyrin, increased with increasing scan number, indicating, that the deposited porphyrin-thiophene copolymer formed a conductive film. Chemical oxidation of H2P12, ZnP12 and CuP12 (Fig. 8), using FeCl3 as oxidant, resulted in the corresponding co-polymers (poly-H2P12, poly-ZnP12 and poly-CuP12) in high yield (> 90 %). The conductivity of the co-polymer poly-H2P12, doped with FeCl3 was found to be over 10−6 S/cm. Increased conjugation between the bithienyl groups and
the porphyrin ring may have caused accelerated energy and electron transfer processes between the porphyrin and oligothiophene units.

The iron(III) porphyrin (**FeP2**, Fig. 2) also undergoes electropolymerisation. An anodic wave at ~1.3 V vs. Ag/AgCl was attributed to oxidation of the peripheral thien-3-yl groups in the monomer and a subsequent single broad anodic wave in the region +1.0 – 1.5 V vs. Ag/AgCl signified polymerisation of a porphyrin film (**poly-FeP2**, Fig. 23) onto the electrode.\(^{32}\) The electrode modified with **poly-FeP2** demonstrated electroactivity due to the presence of the iron (II/III) couple and a mean redox potential of 0.0 V vs. Ag/AgCl suggested a low charge-transfer resistance within the semiconductive film. Bromoiron(III) *meso* tetrakis(thien-3-yl)porphyrin was coordinated with the axial ligand, 1-methylimidazole (im), to form the coordination complex \([\text{Fe(im)P2}]^+\text{Br}^-\). Electrodeposition of the complex resulted in a broad anodic wave in the range +0.8 – 0.15 V vs. Ag/AgCl and the polymerised complex was electroactive with a mean redox potential of +0.05 V vs. Ag/AgCl.

\[
\begin{align*}
\text{Fe(III)P2} & \quad \text{polymn.} \quad \text{poly-FeP2}
\end{align*}
\]

*Figure 23*  
Polymerisation of **FeP2**.
The metalloporphyrins MP60 and MP61 (M = Zn, Pd, Fig. 12) were polymerised by electrochemical oxidative coupling of the meso oligothienyl groups.\textsuperscript{22} The repeated oxidation of meso bithienyl groups of ZnP60 was observed above +1.40 V vs. SCE, with the redox couple of the first oxidation of the porphyrin ring (observed at ca. +1.0 V vs. SCE) increased with increasing number of cycles. Deposition of a polymer (poly-ZnP60) onto the working electrode occurred during the course of the experiment. Electrochemical polymerisation of ZnP61 (oxidation of the porphyrin ring: +0.60 V vs. SCE, oxidative coupling of terthienyl groups: +0.71 - 0.80 V vs. SCE) and the palladium complexes of bithienyl and terthienyl substituted porphyrin was achieved in a similar manner. Infrared analysis indicated that α-α coupling of the meso-oligothienyl groups occur to form a quasi-2D polymer (Fig. 24). Scanning tunnelling microscopy (STM) of an ultra thin film of poly-ZnP61 prepared on a Au(III) substrate confirmed the quasi – 2D structure, although some disorder was included. Film thickness of 0.5 nm indicates a planar orientation of the porphyrin rings, with an alternating structure of porphyrin and oligothiophene moieties. The mean distance between the intersections was ca. 2.82 nm and the model distance between the monomer units was ca. 3 nm which supported the fact that poly-ZnP61 formed a lattice. The d.c. conductivities of poly-ZnP60 and poly-PdP60 were 3 x 10\textsuperscript{-7} S/cm and 2 x 10\textsuperscript{-7} S/cm respectively. Layered polymers cells (ITO electrode/poly-PdP60/poly-ZnP60/Au electrode), constructed by the successive electrochemical polymerisation of PdP60 and ZnP60 showed electric rectifying properties. As the contacts between the individual polymers and the electrodes are ohmic, the rectifying properties are thought to arise from the molecular interface between poly-ZnP30 and poly-PdP60.\textsuperscript{33}
Figure 24  Proposed quasi 2D structures.
2.1.2 Thienyl porphyrins connected through a saturated or conjugated spacer

2.1.2.1 Synthesis

The design and synthesis of a series of thiophene appended porphyrin systems where the thiophene ring is fused to the periphery of the macrocycle via two aza linkages was reported by Crossley and Prashar.\textsuperscript{34} The porphyrin precursors possessed a di-ketone functionality at the $\beta$ position of the macrocycle which was reacted with 3,4-diaminothiophene to produce the laterally conjugated thienyl porphyrins ($\text{H}_2\text{P66} - \text{H}_2\text{P70}$, Fig. 25). The aim was to attach the highly conjugated porphyrin systems to a gold surface through the sulphur atom of the fused thiophene ring in order to study the self assembly and molecular electronic properties of porphyrin based monolayers and thin films.
Figure 25  Crossley and Prasher's fused thiienyl porphyrins $H_2P66 - H_2P70$. 
Ono et al. synthesised a series of naphtoporphyrin systems using a series of pyrroles fused with aromatic rings (isoindole derivatives). The aromatic nitro compound 1, (Scheme 2) was reacted with ethylisocyanoacetate in the presence of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) to give fused pyrrole, 2, in 60% yield. Reduction of 2 to the hydroxymethyl pyrrole, 3, is a crucial step in the reaction. Tetramerisation and oxidation of compound 3 generated the porphyrin $\text{H}_2\text{P71}$. However scrambling led to a mixture of four regioisomers. Only suitably controlled conditions for reduction and tetramerisation allowed the isolation of pure $\text{H}_2\text{P71}$. A similar fused porphyrin-thiophene system ($\text{ZnP72}$, Fig. 26) has also been reported by Callot et al.

![Scheme 2](image1.png)

Scheme 2  Synthesis of P71.

![Figure 26](image2.png)

Figure 26  ZnP72.
3’-[5-(4-Phenoxy)-10,15,20-tritolylporphyrin]-2,2;-bithiophene (H$_2$P73, Fig. 27) and 3’-[5-(4-Phenoxy)-10,15,20-tritolylporphyrin]pentyl-2,2’;5’,2’’-terthiophene (H$_2$P74, Fig. 27) were synthesised by coupling the porphyrin subunit [5-(4-phenoxy)-10,15,20-tritolylporphyrin)] to the relative oligothiophene by a Williamson ether synthesis to yield the tetraphenylporphyrin functionalised bithiophene in 88 % yield and the analogous terthiophene in 73 % yield.$^{37}$ The corresponding cobalt, nickel, zinc, iron and manganese complexes were also produced. In another study 5-(4-(1-hexylthien-3-yl)phenoxy)-10,15,20-tritolylporphyrin (H$_2$P75, Fig. 27) and the corresponding porphyrin without the thienyl group (5-(4-(1-hexyl)phenoxy)-10,15,20-tritolylporphyrin were synthesised by the Adler-Longo method.$^{38}$ The thienyl porphyrin H$_2$P75 was also metallated with nickel in high yield.

\[ \begin{align*}
\text{Figure 27} & \quad \text{P73: } m = 1, n = 0, M = \text{Zn(II)}, \text{Ni(II), Co(II), Fe(III)Cl, Mn(III)Cl} \\
\text{P74: } m = 1, n = 1, M = \text{Ni(II), Co(II), Fe(III)Cl} \\
\text{P75: } m = 0, n = 0, M = 2H, \text{Ni(II)}
\end{align*} \]
On reacting a thiophene substituted benzaldehyde with 5-phenyldipyrromethane, 5,15-bis(4-(2-(3,4-ethylenedioxy)thienyl)phenyl)-10,20-diphenyl porphyrin (H$_2$P76, Fig. 28) and 5,15-bis(4-(2-thienyl)phenyl)-10,20-diphenyl porphyrin (H$_2$P77, Fig. 28) were produced along with their metal analogues in good yield. The thiophene and 3,4-ethylenedioxythiophene moieties were chosen as polymerisation points on the porphyrin monomers as shown in figure 35.

![Porphylin monomers P76 and P77](image)

**Figure 28** Porphylin monomers P76 and P77.

A number of phosphoric, P(V), porphyrin derivatives with two thienylalkoxy or oligothienylalkoxy groups at the axial position of the central metal atom have been synthesised. The donor-photosensitiser-acceptor molecules were synthesised from dichlorophosphoric(V)-tetraphenylporphyrin and the corresponding thienyl or oligothienyl alcohol. Spectroscopic analysis confirmed that the two equivalent alkoxy groups were attached to the central phosphorus atom at the fifth and sixth coordination positions (Fig. 29).
Zinc(II)-porphyrin polymers with meso-linked aryl and ethynyl spacers were synthesised using a combination of Stille and Sonogashira palladium coupling and Ni(cod)$_2$(bpy) coupling techniques. The porphyrin monomers H$_2$P$^1$ – H$_2$P$^5$ were synthesised by the Mac Donald 2+2 reaction of bispyrrole and a range of aldehydes, followed by metallation with zinc yielding ZnP$^1$ – ZnP$^5$ (Fig. 30). The porphyrin monomers were directly coupled to form homopolymers and also coupled to aryl units to form copolymers.
The oligothienyl linkage in multicomponent porphyrin systems is of great importance because it has two roles: it acts as a rigid spacer positioning two neighbouring centres at fixed distance with a well defined geometry, and the spacer can promote electronic communication, thus facilitating electron and/or energy transfer between two porphyrins. For this reason Odobel et al. synthesised a series of oligothiophene bridged bisporphyrins (P86 – P89, Fig. 31). The novel bis-porphyrins are directly substituted at the meso position with an oligothiophene chain tethered by a single, double (trans) or triple bond. The porphyrins were produced by palladium catalysed cross coupling reactions (Stille,
Heck and Sonogashira) between 5-iodo-10,15,20-(3,5-di tert-butylphenyl)porphyrin and the oligothienyl chain. Subsequently either one or both of the linked porphyrins were metallated with zinc.

\[ M = 2\text{H}, 2\text{H}; \text{Zn(II)}, 2\text{H}; \text{Zn(II)}, \text{Zn(II)} \]
\[ L = \text{CH}_2, \quad \text{trans vinyl link}, \quad \text{ethynyl link}. \]

*Figure 31*  
P86: \( n = 0, L = \text{CH}_2 \)
P87: \( n = 1, L = \text{CH}_2 \)
P88: \( n = 1, L = \text{trans vinyl link} \)
P89: \( n = 1, L = \text{ethynyl link} \).

The synthesis of freebase and Zn(II) 5,15-bis(acetylene-4-(ethylenedioxy)thiophene)-10,20-bis(4-methoxycarbonylphenyl)porphyrins (H\(_2\)P90 and ZnP90, Fig. 32) and their hydrophilic disodium dicarboxylate derivatives (H\(_2\)P91 and ZnP91, Fig.32) have also been reported.\(^{43}\) The porphyrin monomer synthesis begins with Sonogashira coupling of 2-iodo-3,4-(ethylenedioxy)thiophene with 3,3-diehtoxypropyne, followed by cyclisation with 5-(4-methoxycarbonylphenyl)dipyrrromethane to give the porphyrin product, H\(_2\)P90, in 3 % yield.
Kuo et al. presented a novel synthetic route to zinc tetrakis(ethynylaryl)porphyrins. Using an adapted Sonogashira method, a range of electron donating substituents were coupled with 5,10,15,20-tetrakis(ethynyl)porphyrin and their redox properties examined. In this manner, zinc(II) 5,10,15,20-tetrakis(ethynylthien-2-yl) porphyrin, ZnP92 was produced (Rxn. 1).
2.1.2.2 Electronic and photophysical properties

The extended $\pi$-system in the porphyrin with fused aromatic rings, $\text{H}_2\text{P71}$ (Scheme 2), causes both the Soret and Q bands to red shift. $^{35}$ The Soret band of $\text{H}_2\text{P71}$ was observed at 432 nm compared to 417 nm for $\text{H}_2\text{TPP}$. In order to compare the extent of $\pi$-conjugation between the porphyrin ring and the fused aromatics the absorbance spectrum of the diprotonated species was obtained. The Soret and Q bands were both red shifted the former more so than the latter. The diprotonated species displays a Soret band $\lambda_{\text{max}}$ at 462 nm with Q bands at 604 and 659 nm. The metallated derivatives were also bathochromically shifted displaying Soret bands at 438 nm and 452 nm for $\text{ZnP71}$ and $\text{NiP71}$ respectively.

Decoupling of the two chromophores by the oxaalkyl spacer was observed in the electronic spectrum of $\text{H}_2\text{P73}$ and $\text{H}_2\text{P74}$ (structures in Fig. 27). $^{37}$ The spectral features consisted of an intense Soret band at 420 nm with Q bands between 510 and 650 nm due to porphyrin transitions and a $\pi-\pi^*$ transition between 290 – 350 nm due to the oligothiophene. The Soret band of $\text{ZnP73}$ was bathochromically shifted by 2 nm compared to its freebase analogue ($\lambda_{\text{max}} = 422$ nm), whereas the $\text{CoP73/74}$ and $\text{NiP73/74}$ derivatives displayed hypsochromically shifted Soret bands at 412 and 416 nm respectively. Spectra of the Fe(III) and Mn(III) complexes showed highly red shifted Soret bands ($\text{Fe(III)P73}$: 511nm, $\text{Fe(III)P74}$: 512 nm, $\text{Mn(III)P73}$: 480 nm) with respect to the freebase porphyrins $\text{H}_2\text{P73}$ and $\text{H}_2\text{P74}$ ($\lambda_{\text{max}} = 420$ nm). An additional intense absorbance between 350 and 400 nm was assigned to charge transfer of occupied $\pi$-orbitals of the porphyrin to vacant d-orbitals of the central metal cation.

The metallated phosphoric(V) porphyrins with axial substituents also displayed a classic porphyrin spectrum with added spectral features due to the axial thienyl moiety at 232, 310 and 357 nm for $\text{P(V)P78}$, $\text{P(V)P79}$ and $\text{P(V)P80}$ (Fig. 29) respectively. $^{40}$ Soret bands were observed at wavelengths of 430, 428 and 431 nm for $\text{P(V)P78}$, $\text{P(V)P79}$ and $\text{P(V)P80}$ respectively with the two Q bands of each porphyrin in the range 558-604 nm. The fluorescence quantum yields and lifetimes in these systems were dependent on the number of thiophene units in the system (Table 6). A decrease of fluorescence lifetime and
quantum yield was observed with an increase in the number of thiophene units. Surprisingly the P(V)P79 system showed a larger decrease in fluorescence lifetime and quantum yield than the P(V)P80 analogue. Fluorescence quenching was observed for P(V)P79 and P(V)P80 compared to diethoxyP(V)tetraphenylporphyrin (τ = 4.4 ns) without thienyl moieties attached, which indicated that photoinduced electron transfer occurred from the oligothiophene moiety to the P(V) porphyrin unit of the 2,2'-bisthiophene and 2',2''':5'',2'''-terthiophene systems.

<table>
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<tr>
<th>Porphyrin</th>
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<th>τ_f (ns)</th>
<th>Φ_f</th>
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<td>613, 668</td>
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<tr>
<td>P(V)P79</td>
<td>615, 668</td>
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<tr>
<td>P(V)P80</td>
<td>622, 673</td>
<td>0.80</td>
<td>3.9 x 10^{-3}</td>
</tr>
</tbody>
</table>

Table 6 Luminescence data for phosphorus porphyrins P78 – P80 in MeCN.^

In the ethynyl-thienyl porphyrin, ZnP92 (Rxn. 1), both the absorbance and emission maxima are bathochromically shifted compared to H2P1 (Fig. 2).^

The electronic spectra of the porphyrin systems connected with four types of oligothiophene bridges (structures in Fig. 31) showed many interesting characteristics.^

The electronic spectra of the porphyrin systems connected with four types of oligothiophene bridges (structures in Fig. 31) showed many interesting characteristics. UV-vis absorbance spectroscopy was used to determine the magnitude of the interporphyrin interactions. The absorbance spectra of ZnZnP86 and ZnZnP87 showed the least perturbation when compared to the reference porphyrin, zinc(II) 5,15-bis(3,5-ditert-butylphenyl)porphyrin. Their spectra were simply the sum of the porphyrin and the oligothiophene bridge indicating that direct attachment of oligothiophene unit to the porphyrin did not perturb the ground state properties. Inserting the vinyl or ethynyl linker between the quaterthiophene moiety and porphyrin core as in ZnZnP88 and ZnZnP89 imparted distinctive features to the absorbance spectra including broadening of the Soret bands.
ZnZnP89 underwent the largest red shift and highest intensification of Q bands within the series. The Soret region of ZnZnP89 was split into two discernible transitions (Fig. 33), at 437 and 448 nm with a shoulder at 417 nm indicative of J-aggregate formation. H2H2P89 and ZnH2P89 displayed single maxima at 442 and 444 nm respectively. Also a 20 % increase in the FWHM of the Soret band in ZnZnP89 was observed compared to the other porphyrins in the P89 series. However, the Q band region of ZnH2P89 is simply the sum of the spectra for ZnZnP89 and H2H2P89. These spectra closely resembled those of structurally similar ethynyl-substituted zinc porphyrins, so the changes seen in the P89 series were attributed to the effect of the ethynyl bridge, without any substantial influence from the quaterthiophene bridge. The changes observed were a result of a decrease in the HOMO-LUMO gap as a consequence of the increased \( \pi \)-conjugation in the system. The smaller vinyl moiety in the bridge of the dyads ZnZnP88, H2H2P88 and ZnH2P88 resulted in Q bands that were also red shifted that can be similarly analysed. Thus, both vinyl or ethynyl substitution (P88 and P89) at the meso-position gave rise to enhanced coupling between the two porphyrin units in comparison to the directly linked quaterthiophene bridge (P86 and P87) which displayed weak interaction indicating only slight perturbation of the ground state properties of the porphyrin units. Similar to the absorbance spectra, the fluorescence spectra are altered by the nature of the bond linking the porphyrin units to the bis- or quaterthiophene bridge (Table 7). The fluorescence quantum yields for the zinc dyads increase in the order ZnZnP87 < ZnZnP86 < ZnZnP88 \( \approx \) ZnZnP89. The fluorescence quantum yields for the H2H2 porphyrin series followed a similar trend. The largest Stokes shifts between were observed for the vinyl series, P88, indicating that the dyads undergo a significant reorganisation of nuclear coordinates in the excited state. The energy transfer in the asymmetrical dyads was also studied by fluorescence spectroscopy. Photoinduced energy transfer between asymmetrical ZnH2 porphyrins was investigated. The lowest excited singlet state of the zinc porphyrin was higher than that of the corresponding freebase porphyrin. Excitation of the asymmetrical dyad at 560 nm (the wavelength at which most light is absorbed by the zinc porphyrin) produced a fluorescence spectra with > 95 % emission from the freebase porphyrin. The fluorescence of the zinc porphyrin was almost completely turned off in each of the ZnH2 systems and fluorescence occurred from the freebase porphyrins. This indicated efficient energy transfer from the zinc porphyrin excited state to the nearby freebase porphyrin. The decrease in the zinc porphyrin fluorescence lifetime indicated a clear trend in energy
transfer from the slowest to the fastest of the order $\text{ZnH}_2\text{P}87 \approx \text{ZnH}_2\text{P}88 > \text{ZnH}_2\text{P}86 > \text{ZnH}_2\text{P}89$.

Figure 33  **Electronic absorbance spectra of ZnZnP86, ZnZnP87, ZnZnP88 and ZnZnP89 and zinc monomeric reference porphyrin in CH$_2$Cl$_2$**
<table>
<thead>
<tr>
<th>Porphyrin</th>
<th>$\lambda_{em}$ (nm)</th>
<th>$\tau_f$ (ns)</th>
<th>$\Phi_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnZnP86</td>
<td>624</td>
<td>1.60</td>
<td>0.10</td>
</tr>
<tr>
<td>ZnH$_2$P86</td>
<td>664</td>
<td>0.02</td>
<td>0.86</td>
</tr>
<tr>
<td>H$_2$H$_2$P86</td>
<td>662</td>
<td>3.90</td>
<td>0.86</td>
</tr>
<tr>
<td>ZnZnP87</td>
<td>626</td>
<td>1.30</td>
<td>0.09</td>
</tr>
<tr>
<td>ZnH$_2$P87</td>
<td>666</td>
<td>0.03</td>
<td>0.78</td>
</tr>
<tr>
<td>H$_2$H$_2$P87</td>
<td>667</td>
<td>3.50</td>
<td>0.78</td>
</tr>
<tr>
<td>ZnZnP88</td>
<td>676</td>
<td>1.30</td>
<td>0.17</td>
</tr>
<tr>
<td>ZnH$_2$P88</td>
<td>713</td>
<td>0.03</td>
<td>0.21</td>
</tr>
<tr>
<td>H$_2$H$_2$P88</td>
<td>717</td>
<td>3.40</td>
<td>0.22</td>
</tr>
<tr>
<td>ZnZnP89</td>
<td>657</td>
<td>1.40</td>
<td>0.18</td>
</tr>
<tr>
<td>ZnH$_2$P89</td>
<td>688</td>
<td>0.01</td>
<td>0.31</td>
</tr>
<tr>
<td>H$_2$H$_2$P89</td>
<td>690</td>
<td>6.20</td>
<td>0.34</td>
</tr>
</tbody>
</table>

Table 7 Luminescence data for porphyrin dimers P86 – P89 in THF.\(^{42}\)

A Soret band $\lambda_{max}$ at 460 nm was observed for ZnP90 (Fig. 32) in dichloromethane, while poly-ZnP91 displayed a hypsochromically shifted Soret band at 434 nm in dimethylsulfoxide.\(^{43}\) An intense single fluorescence peak was observed at 720 nm for ZnP90 whereas poly-ZnP90 and poly-ZnP91 produced two fluorescence bands at 650, 720 nm and 620, 660 nm respectively.

Electronic coupling between the adjacent porphyrin units in the polymer backbone of poly-ZnP84 and poly-ZnP85 (Fig. 30) resulted in splitting of the Soret band in the UV-vis spectra (Table 8).\(^{41}\) The monomer ZnP81 showed a sharp Soret peak at 417 nm with FWHM of ca. 20 nm. Polymers poly-ZnP81, poly-ZnP83, poly-ZnP84 and poly-ZnP85 gave peaks in the Soret and Q band region, the sharpness and intensity of which depended on the structure of the polymer. Poly-ZnP85 with an ethynyl spacer directly bound to the meso position of the porphyrin ring displayed the largest shift for all Soret bands in the series. Polymers which have a spacing thiophene unit directly bonded to the zinc porphyrin units, such as poly-ZnP81, poly-ZnP83 and poly-ZnP84 (Fig. 30) display two emission peaks similar to those of the relative monomers. In accord with its UV-vis
spectrum, the photoluminescence of poly-ZnP85 was at a longer wavelength than the other polymers.

<table>
<thead>
<tr>
<th>Porphyrin</th>
<th>(\lambda_{\text{max}}) Soret (nm)</th>
<th>(\lambda_{\text{max}}) Q bands (nm)</th>
<th>(\lambda_{\text{ex}}) (nm)</th>
<th>(\lambda_{\text{em}}) (nm)</th>
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</thead>
<tbody>
<tr>
<td>ZnP81</td>
<td>417</td>
<td>542, 583</td>
<td>417</td>
<td>592, 644</td>
</tr>
<tr>
<td>Poly-ZnP81</td>
<td>416</td>
<td>543, 582</td>
<td>416</td>
<td>590, 642</td>
</tr>
<tr>
<td>Poly-ZnP83</td>
<td>416</td>
<td>546, 584</td>
<td>416</td>
<td>590, 639</td>
</tr>
<tr>
<td>Poly-ZnP84</td>
<td>417, 431</td>
<td>547, 585</td>
<td>422</td>
<td>591, 646</td>
</tr>
<tr>
<td>Poly-ZnP85</td>
<td>454, 490</td>
<td>697</td>
<td>455</td>
<td>724</td>
</tr>
</tbody>
</table>

*Table 8*  
Electronic data for P81 – P85 in CHCl₃.⁴¹
2.1.2.3 Electrochemical properties and electropolymerisation

HOMO-LUMO energy gaps of 2.06 and 2.01 eV vs. SCE were calculated for ZnP71 and NiP71 (Scheme 2) respectively. These values correspond to a reduced HOMO-LUMO energy gap of almost 30 eV relative to ZnTPP. Cyclic voltammetry studies carried out on H2P73 and H2P74 (Fig. 27) reveal potentials comparable to the individual subunits which are in agreement with the UV-vis studies, confirming a lack of electronic communication. Polymerisation of the freebase porphyrin monomer units, H2P73 and H2P74, was not possible due to the interference of the porphyrins internal nitrogens with the oligothiophene radical cations. However electrochemical oxidation of the metallo-porphyrins lead to the corresponding porphyrin functionalised polythiophene. The metallo-bithiophene analogue M(II)/M(III)P73, showed a higher tendency to polymerise and gave thicker films. Only Mn(II)P73 displayed low polymerisation trends. Electrochemical studies on the polymers displayed a combination of reversible redox waves for the conducting polythiophene backbone and the porphyrin redox centres (Table 9). Reduction of the metal centres of the porphyrin units at negative potentials was not observed due to the insulating character of the polythiophene backbone in the potential window monitored.
<table>
<thead>
<tr>
<th>Porphyrin Reduction (V)</th>
<th>Metal Cation (V)</th>
<th>Porphyrin Oxidation (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂P73</td>
<td>-2.03</td>
<td>-1.71</td>
</tr>
<tr>
<td>H₂P74</td>
<td>-2.05</td>
<td>-1.70</td>
</tr>
<tr>
<td>Co(II)P73</td>
<td>-1.95</td>
<td>----</td>
</tr>
<tr>
<td>Co(II)P74</td>
<td>-1.95</td>
<td>----</td>
</tr>
<tr>
<td>Ni(II)P73</td>
<td>----</td>
<td>-1.81</td>
</tr>
<tr>
<td>Ni(II)P74</td>
<td>----</td>
<td>-1.80</td>
</tr>
<tr>
<td>Fe(III)P73</td>
<td>----</td>
<td>-1.60</td>
</tr>
<tr>
<td>Fe(III)P74</td>
<td>----</td>
<td>-1.57</td>
</tr>
<tr>
<td>Mn(III)P73</td>
<td>-2.14</td>
<td>----</td>
</tr>
<tr>
<td>Zn(II)P73</td>
<td>----</td>
<td>-1.92</td>
</tr>
</tbody>
</table>

Table 9  Redox potentials of P73 – P74 in CH₂Cl₂ vs. Fc/Fc⁺.³⁷

In contrast, Ballarin et al. observed irreversible oxidation of the porphyrin moiety in a copolymer of H₂P73 and the tetraphenylporphyrin-alkoxy-monothiophene unit, H₂P75.³⁸a In a later study,³⁸b the authors also investigated the nickel derivative, NiP73, and analysed the complexation ability of the porphyrin unit in the polymer chain. Both H₂P73 and NiP73 formed mechanically stable electrode surface films. For H₂P73, the oxidation process centred at +1.04 V vs. SCE, previously ascribed to the oxidation of the porphyrin-containing monomer, was observed along with an additional redox couple in the potential region +0.45 - 0.70 V vs. SCE attributed to oxidation of the co-polymer. Analysis of NiP73 was quite different. The oxidation process recorded for H₂P73 was no longer
present and a reversible system was evident with an oxidation potential of +0.94 V vs. SCE. This shift with respect to $H_2P73$ was attributed to the nickel porphyrin core, however the highly distorted conformation of the porphyrin ring induced upon nickel(II) complexation should also be considered.

Electrochemical oxidation of $P(V)P79$ and $P(V)P80$ (Fig. 32) resulted in the formation of one dimensional polymers (Fig. 34).\textsuperscript{40} $\text{Poly-}P(V)P79$ and $\text{poly-}P(V)P80$ were deposited onto the electrode as peak currents assigned to the redox reaction of the $P(V)$ porphyrin increased. $\text{Poly-}P(V)P80$ displayed a new anodic peak due to the oxidation of sexithiophene. The UV-vis absorbance of the bithiophene and terthiophene moieties ($\lambda_{\text{max}} = 310, 357$ nm respectively) disappeared upon polymerisation with strong quenching of the fluorescence in the polymers. In addition conductivities of $\text{poly-}P(V)P79$ and $\text{poly-}P(V)P80$ were strongly enhanced by photoirradiation.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{polythiophene_chain.png}
\caption{Polymeric oligothiophene chain of $P(V)$-tetraphenylporphyrins.}
\end{figure}

Zinc(II) 5,15-bis(4-(thien-2-yl)phenyl)-10,20-diphenylporphyrin ($\text{ZnP76}$) failed to form a polymer owing to its low solubility in a range of solvents.\textsuperscript{39} Polymeric films of $\text{ZnP77}$ (Fig. 35) were deposited on an array of electrodes in several solvents by electrochemical oxidation. During the polymerisation process, the polymer film remained electroactive indicating, that the film itself, has enough electrical conductivity to maintain the polymer growth process. An electrode modified with the $\text{poly-}\text{ZnP77}$ exhibited two reversible one-electron porphyrin ring oxidations at +0.78 and +1.06 V vs. Ag/AgCl. With potential scan rates of 60-180 mV/s, the potential difference between oxidation and reduction peaks ($\Delta E_p$)
was 50-100 mV, which indicated the high electroactivity of the porphyrin film. Deposited polymer layers ranging from $5 \times 10^{-10}$ to $5 \times 10^{-6}$ mol/cm$^2$ were reproducible. The synthesised polymer, **poly-ZnP77**, was considered to be two isolated redox systems: the porphyrin and the 5,5'bisphenyl-2,2'-bi(3,4-ethylene-dioxy-thiophene). Oxidation of the thienyl subunit occurred at +0.61 V vs. Ag/AgCl, cathodic of the porphyrin unit (+0.78 and +1.06 V vs. Ag/AgCl). Consequently the thienyl subunit in **poly-ZnP77** was only electroactive after oxidation of the porphyrin ring and as a result the oxidised state of the bithiophene subunit was trapped when the potential scan was reversed. The formation of two distinct redox units in the polymer chain, **poly-ZnP77**, was believed to be responsible for the observed charge trapping phenomenon, the mechanism for which was supported using model compounds.

**Figure 35** **poly-ZnP77**.

Polymerisation of the **ZnP90** and **ZnP91** complexes to their respective homopolymers was carried out by electrochemical oxidation.$^{43}$ The monomers were also successfully polymerised by chemical oxidation with iron(III)chloride. Cyclic voltammetry on **poly-ZnP90** reveals a zinc porphyrin oxidation in the range +0.6 – 0.9 V vs. Ag/AgCl while oxidation of the thiophene moiety was observed at higher potentials (>1.0 V vs. Ag/AgCl). Conductivity measurements of the hydrophobic zinc porphyrinate polymer **poly-ZnP90** on platinum electrodes gave upper values of $6 \times 10^{-3}$ S/cm. Images of the sodium derivative of the zinc(II) polymer, **poly-ZnP91** (Fig. 36), were recorded by TEM and AFM. The
formation of uniform porphyrin wires of up to 2.5 µm in length (ca. 1200 monomer units) was confirmed, with a thickness of ca. 2 nm corresponding to the width of the porphyrin unit.

*Figure 36 poly-ZnP91.*
2.1.3 Applications

The various uses of porphyrins are widely studied and include such areas as catalytic, therapeutic and potential (opto-)electronic applications. Extended π-conjugated porphyrin systems are increasingly investigated due to their applications towards advanced technologies, which include nonlinear optical materials. By appending various chemical moieties onto the periphery of the porphyrin ring (e.g. functionalised thiophenes) the electronic and redox properties of the macrocycle in such systems can easily be modulated. Also varying the metal centre of the porphyrin allows these properties to be fine tuned. Desirable molecular and material properties, such as large hyperpolarisabilities, can therefore be imparted onto the porphyrin ring by appropriate substitution and metallation.

Their strong absorbance and fluorescence properties allow porphyrins wide used in (opto-) electronic systems. Redox control of meso zinc(II) trithienyl and triphenylporphyrin – ferrocene dyads (ZnP27 and ZnP28, Fig. 37) allowed the on/off switching of porphyrin fluorescence through use of the ferrocene/ferricenium redox couple. Quenching of the porphyrin fluorescence by excited-state electron transfer from the ferrocene to the porphyrin was easily reversed by oxidation to the ferricenium ion allowing the porphyrin fluorescence to be “switched on”. The reversible “on” and “off” switching of the electron-transfer pathway allows for efficient control of the porphyrin luminescence.

Figure 37 On/off switching of porphyrin fluorescence in ZnP27 and ZnP28+.
Electrochemical studies of the thienyl porphyrins, \( \text{ZnP21} - \text{ZnP26} \) (Fig. 10) have shown that the band gap can be controlled by varying the number of thienyl substituents on the porphyrin ring and by the nature of the thienyl moiety itself (e.g. thiophene vs. bromothiophene). As previously discussed, the reduction in band gap followed the order \( \text{ZnP22} \) (2.02 eV), \( \text{ZnP26} \) (2.02 eV), \( \text{ZnP25} \) (2.04 eV), \( \text{ZnP24} \) (2.06 eV) and \( \text{ZnTPP} \) (2.09 eV). Thus, through molecular design, the application of thienyl porphyrins in (opto-)electronics such as dye sensitised solar cells and photovoltaic devices becomes a real possibility.

Supramolecular systems with magnesium \textit{meso} tetrakis(thien-2-yl)porphyrin, (\text{MgP1}, Fig. 2) and \( \beta \)-cyclodextrins have been produced.\(^{49}\) In a phosphate buffer solution of pH 5.4, \text{MgP1} was found to form 1:1 supramolecular systems with \( \beta \)-cyclodextrin and four other modified \( \beta \)-cyclodextrins. The cyclodextrin cavity offered a hydrophobic environment for guest molecules with two of the modified cyclodextrins, dimethoxy-\( \beta \)-cyclodextrin (DM-\( \beta \)-CD) and trimethoxy-\( \beta \)-cyclodextrin (TM-\( \beta \)-CD), substantially increasing this hydrophobic environment. A bathochromic shift and decrease in extinction coefficient of the Soret band of \text{MgP1}, was observed upon formation of a supramolecular system of \( \beta \)-cyclodextrins with \text{MgP1}. When fluorescent substances move from a polar phase to a non-polar phase, the quantum efficiency of fluorescence increases. An enhancement in emission intensity and shift to shorter wavelength was noted for the DM-\( \beta \)-CD/\text{MgP1} and TM-\( \beta \)-CD/\text{MgP1} systems, indicative of the formation of supramolecular systems. These results showed that the modified \( \beta \)-cyclodextrins easily formed a supramolecular system with \text{MgP1}.

The \textit{poly-FeP2} modified electrode is the first all-synthetic electrochemical sensor for the superoxide anion radical (\( \text{O}_2^-\)) due to its efficient electrocatalytic oxidation of \( \text{O}_2^-\) to \( \text{O}_2 \). To mimic the iron centre of cytochrome-\( \text{c} \), an iron(III) porphyrin modified electrode was developed by Yausa et al.\(^{50}\) The \([\text{Fe(im)P2}]^+\text{Br}^-\) electrode was applied to detect \( \text{O}_2^-\) and results indicated that \( \text{O}_2^-\) was catalytically oxidised at the modified electrode. The axial imidazole ligand enables the oxidation of \( \text{O}_2^-\) by an outer-sphere process comparable to cytochrome-\( \text{c} \) mediated \( \text{O}_2^-\) oxidation. The sensitivity of the system towards \( \text{O}_2^-\) is 50
times higher than that obtained in a previous study using a modified cytochrome-c/Au electrode (typically ~6 nA µM⁻¹ cm⁻²).

Mono substituted porphyrins (ZnP19 and ZnP20, Fig. 8) with meso 5-membered heteroaromatic groups were designed to evaluate the effects of the spacer on mesoporous TiO₂ nanoparticle films.¹⁷ The carboxylic group ensured a single point of attachment to the surface. The three remaining mesityl meso substituents possess large steric bulk, reducing aggregation of the porphyrin molecules. Porphyrin – modified ITO/TiO₂ electrodes were produced by adsorbing the porphyrin onto the prepared ITO/TiO₂ electrode. ZnP19 adsorbed quickly and formed a densely packed porphyrin monolayer whereas ZnP20 adsorbed at a slower rate and formed a loosely packed monolayer. Total amounts of porphyrin adsorbed onto the TiO₂ film were calculated using surface area on the electrode and porphyrin densities. ZnP19 was found to have a small density value of 2.0 x 10⁻¹¹ mol cm⁻² while ZnP20 possessed a value of 1.2 x 10⁻¹⁰ mol cm⁻². The calculated porphyrin density value together with the tilt of the molecules is responsible for the packing on the surface. ZnP20 was tilted almost parallel to the TiO₂ surface and so adsorbed in a tightly packed monolayer whereas ZnP19’s horizontal orientation of the acid group resulted in a loosely packed monolayer. An ITO/TiO₂/porphyrin dye sensitised solar cell device sensitised with ZnP19, was found to possess high photovoltaic properties with maximum incident photon-to-current-efficiency (IPCE) of 65 % and maximum power conversion efficiency (ηmax) of 3.1 %. Values of IPCEmax = 34 % and ηmax = 2.0 % were obtained for ZnP20. The higher effectiveness of ZnP19 is attributed to the additional electron-transfer pathway through specific interaction between the sulphur atom in the bridge and the TiO₂ surface.

Friedlein et al. reported the self-assembly of supramolecular columns of large polycyclicaromatic hydrocarbons and thienyl porphyrins.⁵¹ Ordered films of porphyrins with functional side arms (e.g. thiophene) are ideal for (opto-)electronic applications, where fast charge separation and transport are required. ZnP21 (Fig. 6) was used for this “bottom-up” synthetic strategy of a highly ordered nanostructure at a molybdenum disulfide (MoS₂) surface. Bromination of the peripheral 5’-position of the thiophene
increased solubility and facilitated the self assembly of the columnar nanostructures in solution. Tapping-mode scanning force microscopy (TM-SFM) indicated the film was flat (10 nm thick, ±2 nm) and the surface was completely covered. Photoelectron spectroscopy was used to investigate the alignment of the nanostructures on the surface. Spectral changes observed upon annealing were attributed to increased structural order in the columnar arrangements. Cone-like photoelectron emission around the molecular axis (typical for π-electronic states of discotic molecules) indicated a flat orientation of the porphyrin rings, face to face with the surface substrate. The alignment of the columns is suited for solar cell applications.

The non-linear optical properties viz. the molecular first hyperpolarisability, β, was evaluated using femtosecond hyper-Rayleigh scattering (fs-HRS) pulsed laser measurements for a range of thienyl systems (ZnP29 – ZnP38, Fig. 11). Exceptionally large dynamic hyperpolarisability values of 670 – 4350 x 10^{-30} esu were obtained at 1300 nm incident irradiation. The value of 4350 x 10^{-30} esu, obtained for ZnP31, was the largest β_{1300} value (measured at 1300 nm incident radiation) for an uncharged chromophore. Using the same technique the molecular first hyperpolarisability values of ZnP35 – ZnP38 (Fig. 11) were determined. ZnP35’s formyl group drove a blue shift in the Q band (λ_{max} = 676 nm), whereas ZnP36’s strong dicyanovinyl acceptor caused a red shift in the Q band position (λ_{max} = 698 nm) relative to ZnP32 (λ_{max} = 685 nm). Compounds ZnP37 and ZnP38 were analogues of ZnP32 in which there was an inversion of charge-transfer direction. ZnP38 showed diminished excited-state structural heterogeneity relative to ZnP32 and ZnP37, caused by the planarity of the conjugated carbazolyl unit. As a result both ZnP37 and ZnP38 β_{1300} values (Table 4) exceeded that measured for ZnP32, but interestingly, ZnP38 exceeded that of ZnP32 and ZnP35, approximately 2-fold. These enhanced results indicated that further improvements in the already large magnitude for β_{1300} values within the porphyrin-oligothiophene based neutral dipolar chromophores should be possible.

A copolymer of H_2P18 (Fig. 7) and terthiophene, poly-H_2P18 (Fig. 38), was the basis for a novel photoelectrochemical cell. The use of a porphyrin co-polymer enhanced the light
harvesting capabilities of a previously synthesised polythiophene-based photovoltaic device. Scanning electron microscopy of poly-$H_2P18$ showed an open porous morphology (Fig. 39) which was beneficial for photovoltaics due to the larger surface area. A series of porphyrin to terthiophene monomer mole ratios were also investigated and equimolar amounts of each were found to give the best energy conversion results. This photovoltaic device had an energy conversion efficiency of 0.09%. An additional increase (0.06 – 0.12%) was also observed in the efficiency of the copolymer after soaking in a zinc(II) solution due to metallation of ca. 25% of the porphyrin units on the polymer backbone.

**Figure 38** Poly-$H_2P18$. 

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Figure 39  Scanning electron micrograph of poly-H$_2$P18.$^{52}$
2.2 Abstract

The aim of this chapter is to gain information about the variability of the general types of spectra in connection with the variability of the structure in thienyl porphyrins. To date, there is still much discussion about the changes observed in the spectra of thienyl porphyrins. The question remains - are the changes observed in the spectra a result of the increased conjugation induced upon thienyl substitution of the porphyrin ring or a result of the conformation which the meso thienyl substituents adopt?

Historically, bathochromically shifted absorbance and emission spectra were attributed to the inductive effect of the meso thienyl moiety. However investigations carried out by Rochford et al. and Brückner et al. indicated that this explanation was over simplified. Rochford et al. synthesised a range of thienyl porphyrins (Fig. 9) which were compared to ZnTPP. For the tetra substituted thienyl porphyrins both the absorbance and emission spectra were red shifted were compared to ZnTPP. By varying the number of thienyl rings and their substituents, the overall effect of the substitution pattern could be observed. Successive replacement of a phenyl ring with a thien-2-yl ring which had an ethynyltrimethylsilyl moiety at the thien-5-yl position resulted in sequential red shifts of 4 nm in the absorbance spectra for each ring replaced. The authors attributed the shifts to increased coupling of the overlapping $\pi$ systems of the porphyrin and thiophene rings. Evidence for this included an increase in the FWHM of the porphyrin Soret band.

Brückner and co workers synthesised thienyl porphyrins with a methyl group attached at various position on the thienyl ring (Fig. 16). Changes observed in the spectra indicated that the position of substituents on the meso thienyl groups had a direct influence on the electronic properties of the porphyrin ring. Subsequently, DFT was used to calculate the conformation which the thienyl rings adopted with respect to the porphyrin macrocycle. The results showed that the thienyl rings adopted a co-planar arrangement which may allow for greater $\pi-\pi$ orbital overlap between the thienyl group and the porphyrin macrocycle.
Thus a series of meso tetra (thien-2-yl)porphyrins and meso tetra (phenyl)porphyrins were produced, each further substituted with ethynylbenzene, ethynylthien-2-yl or ethynylthien-3-yl moieties (Fig. 40).

![Diagram of porphyrins produced for this study.](image)

*Figure 40* Porphyrins produced for this study.
Porphyrsins NB-ZnP1 – NB-ZnP3 were synthesised with substituents at the thien-5-yl position, in order to examine whether an additional aryl group would cause further coupling of the overlapping $\pi$ systems and if so, the effect of the choice of aryl ring. Porphyrsins NB-ZnP4 and NB-ZnP5 possess the same terminal substituents (ethynylbenzene and ethynylthien-2-yl) as NB-ZnP1 and NB-ZnP2; however they are substituted at the thien-4-yl position. NB-ZnP4 and NB-ZnP5 can therefore be compared directly to NB-ZnP1 and NB-ZnP2 in order to examine how the conjugation pathway affects the spectra of porphyrin. Porphyrsins NB-ZnP6 and NB-ZnP7 are phenyl substituted porphyrsins which have been further substituted at the para position with ethynylthien-2-yl and ethynylthien-3-yl moieties respectively. These porphyrsins can be compared NB-ZnP2 and NB-ZnP3 as they possess the same terminal substituents. However, the phenyl porphyrsins, NB-ZnP6 and NB-ZnP7, should adopt an idealised orthogonal arrangement with respect to the porphyrin plane. Thus, as the $\pi$ systems of the porphyrin and meso substituents will no longer be overlapping any changes observed in the spectra can be attributed to the conformation rather than the coupling of the $\pi$ systems.

Increased FWHM of the porphyrin Soret band is evidence of increased coupling of the overlapping $\pi$ systems, thus UV-vis absorbance spectra shall be obtained to investigate the extent of this overlap. Emission spectra and lifetimes of the porphyrsins may indicate how substitution pattern affects the singlet and triplet excited states that are formed following absorbance. Electrochemistry may provide information about the general excited states of the porphyrsins under study relative to each other and ZnTPP.

For NB-ZnP1 – NB-ZnP3, substitution at the thien-5-yl position of the meso thienyl substituent would be expected to increase conjugation within the macrocycle. Therefore, bathochromic shifts in the absorbance and emission spectra are expected. The effective conjugation for NB-ZnP4 and NB-ZnP5 should be lower than in NB-ZnP1 – NB-ZnP3 and therefore modest spectral shifts are expected with respect to ZnTThP. Porphyrins NB-ZnP6 and NB-ZnP7 have a phenyl ring attached to the porphyrin macrocycle so the properties of these porphyrsins are expected to be more like ZnTPP. However the effect of terminal thienyl moiety can be examined by changes in the electronic properties.
2.3 Experimental

2.3.1 Materials

All operations were carried out under an atmosphere of argon or nitrogen using standard Schlenk techniques. All solvents were supplied by the Aldrich Chemical Company. Dichloromethane was dried over MgSO\(_4\) prior to use. Methanol was distilled over magnesium turnings and iodine before use. All organic reagents were purchased from the Aldrich Chemical Company. Benzaldehyde, 5-bromo-2-thiophencarboxaldehyde and 4-bromo-2-thiophencarboxaldehyde were distilled using a Buchi Kügelrohr apparatus prior to use. Pyrrole was freshly distilled over potassium hydroxide before use. Anhydrous triethylamine, 1-phenylacetylene, 2-ethylthiophene, 3-ethylthiophene, 2-thiophencarboxaldehyde, 4-bromobenzaldehyde, propionic acid, boron trifluoride diethyletherate and \(p\)-chloranil were all used without further purification. Bis(triphenylphosphine)palladium(II)chloride, triphenylphosphine and cuprous iodide were used as received in the coupling reactions. These reagents undergo in-situ formation of Pd(PPh\(_3\))\(_4\). Column chromatography was carried out using neutral silica gel (Merck, used as received). All mobile phases for column chromatography were dried over MgSO\(_4\) prior to use. Solvents used in emission and lifetime measurements were of spectroscopic grade and used without further purification. All solvents were deoxygenated by purging with argon or nitrogen for ~10 minutes. The preface “NB-” is applied to compound codes indicating that these are novel compounds synthesised throughout this work.

2.3.2 Equipment

All syntheses involving air- and moisture-sensitive reagents were performed in oven or flame dried glassware. NMR spectra were recorded on a Bruker model AC 400 MHz spectrometer and Bruker model ANC 600 MHz spectrometer using CDCl\(_3\) as solvent. All NMR spectra were calibrated according to the residual solvent peak, i.e. CHCl\(_3\) at 7.26 ppm for all \(^1\)H spectra and 77.16 ppm for all \(^13\)C spectra. Chemical shifts (\(\delta\)) are given in parts per million (ppm). Proton coupling constants (\(J\)) are given in Hertz (Hz). Melting points were measured on a Stuart Scientific SMP1 melting point apparatus. IR spectra were recorded on a Perkin-Elmer 2000 FT-IR spectrometer (2 cm\(^{-1}\) resolution) in a 0.1 mm sodium chloride liquid solution cell using spectroscopic grade dichloromethane. All UV-
vis spectra were measured on an Agilent Technologies 8453 photodiode array spectrometer using a 1 cm$^3$ quartz cell. Emission spectra (accuracy ± 5 nm) were recorded at 298 K using a LS50B luminescence spectrophotometer, equipped with a red sensitive Hamamatsu R928 PMT detector, interfaced with Elonex PC466 employing Perkin-Elmer FL WinLab custom built software. Luminescence lifetime measurements were made using an Edinburgh Analytical Instruments (EAI) Time-Correlated Single Photon Counting apparatus (TCSPC) as described by Browne et al.$^{53}$ Cyclic voltammetry experiments were carried out using a CH instrument model 600a electrochemical workstation at a scan rate of 0.1 VS$^{-1}$. Electrochemical studies were conducted using a conventional three electrode system consisting of a 2 mm diameter Teflon shrouded glassy carbon working electrode, a platinum wire auxiliary electrode and a saturated calomel reference electrode. The solvent used in all experiments was spectrophotometric grade dichloromethane and the supporting electrolyte was 0.1 M TBAPF$_6$. Deoxygenation of the solutions was achieved by bubbling through nitrogen for approximately 10 minutes and a blanket of nitrogen was maintained over the solution during all experiments.
2.3.3 Synthesis
2.3.3.1 Procedure for the preparation of aldehydes via the Sonogashira reaction

To a flame dried round bottom flask anhydrous triethylamine (~30 ml) was added and purged with nitrogen for 10 minutes. Following this, the appropriately substituted halogenated thiophenecarboxaldehyde was added and the solution was purged for a further 5 minutes. A catalytic quantity of bis(triphenylphosphine)palladium(II)chloride, triphenylphosphine and cuprous iodide were added to the flask followed by an excess of aryl alkyne in quick succession. The reaction mixture was refluxed overnight under an inert atmosphere and then allowed to cool. Excess aryl alkyne and solvent was removed under reduced pressure. The crude product was extracted from the brown oil by first adding ca. 5 ml of dichloromethane followed by the addition of ca. 25 ml of petroleum ether (or hexane). The solvent layer was then decanted off. This process was repeated several times until the washings remained colourless. The washings were combined and dried over magnesium sulphate. The solvent was then removed via rotary evaporation affording a dark viscous oil. The crude product was then purified using a Kügelrohr or by column chromatography as described for each compound.
2.3.3.1.1 5-(Phenylethynyl)thiophene-2-carboxaldehyde (A1)

5-Bromothiophene-2-carboxaldehyde (6.0 mmol, 0.71 ml), bis(triphenylphosphine) palladium(II)chloride (0.12 mmol, 84 mg, 2 %), triphenylphosphine (0.24 mmol, 63 mg, 4%), cuprous iodide (0.12 mmol, 23 mg, 2 %) and 1-phenylacetylene (9.0 mmol, 0.99 ml) were used. The crude product was purified using a Kügelrohr (240 °C, 0.04 mmHg) which afforded a bright yellow solid. Yield: 102 mg, 4.8 mmol, 80 %. Spectroscopic data were in good agreement with reported data.\textsuperscript{55}

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): 9.86 (1H, s), 7.67 (1H, d, \textit{J} = 3.6 Hz), 7.55-7.52 (2H, m), 7.39-7.37 (3H, m), 7.31 (1H, d, \textit{J} = 3.6 Hz) ppm. \textbf{m.p.} = 89 - 90 °C.
5-Bromothiophene-2-carboxaldehyde (3.0 mmol, 0.36 ml), bis(triphenylphosphine)palladium(II)chloride (0.18 mmol, 126 mg, 6%), triphenylphosphine (0.36 mmol, 94 mg, 12%), cuprous iodide (0.18 mmol, 34 mg, 6%) and 2-ethynylthiophene (3.3 mmol, 0.35 ml) were used. The crude product was purified by column chromatography on silica gel using CH$_2$Cl$_2$: hexane (50:50) as mobile phase which afforded an orange-yellow solid. Yield: 455 mg, 2.08 mmol, 69%. Spectroscopic data were in good agreement with reported data.$^{55b}$

$^1$H NMR (400 MHz, CDCl$_3$): 9.87 (1H, s), 7.68 (1H, d, $J = 4.0$ Hz), 7.39-7.38 (1H, m), 7.36-7.35 (1H, m), 7.31 (1H, d, $J = 4.0$ Hz), 7.06-7.04 (1H, m) ppm. m.p. = 78 - 79 ºC.
5-(Thien-3-ylethynyl)thiophene-2-carboxaldehyde (NB-A3)

5-Bromothiophene-2-carboxaldehyde (1.5 mmol, 0.18 ml), bis(triphenylphosphine) palladium(II)chloride (0.6 mmol, 63 mg, 6 %), triphenylphosphine (0.18 mmol, 47 mg, 12 %), cuprous iodide (0.09 mmol, 17 mg, 6 %) and 3-ethynlthiophene (1.65 mmol, 0.16 ml) were used. The crude product was purified by column chromatography on silica gel using CH$_2$Cl$_2$ : hexane (50 : 50) as mobile phase which afforded a yellow solid. Yield: 245 mg, 1.12 mmol, 75 %.

$^1$H NMR (400 MHz, CDCl$_3$): 9.86 (1H, s), 7.66 (1H, d, $J = 4$ Hz), 7.61-7.60 (1H, m), 7.34-7.32 (1H, m), 7.29 (1H, d, $J = 4$ Hz), 7.21-7.20 (1H, m) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): 182.40, 143.78, 136.09, 132.91, 132.37, 130.25, 129.61, 125.92, 121.00, 93.19, 81.63 ppm. IR (CH$_2$Cl$_2$): (C=O) 1671 cm$^{-1}$, (C≡C) 2209 cm$^{-1}$. m.p.: 92 – 93 ºC.
2.3.3.1.4 4-(Phenylethynyl)thiophene-2-carboxaldehyde (NB-A4)

4-Bromo-2-thiophenecarboxaldehyde (2.6 mmol, 500 mg), bis(triphenylphosphine) palladium(II)chloride (0.16 mmol, 112 mg, 6%), triphenylphosphine (0.31 mmol, 81 mg, 12%), cuprous iodide (0.16 mmol, 30 mg, 6%) and 1-phenylacetylene (3.27 mmol, 0.34 ml) were used. The crude product was purified by column chromatography using silica gel and CH$_2$Cl$_2$ : hexane (40:60) as mobile phase which afforded a bright yellow solid. Yield: 502 mg, 2.36 mmol, 91%.

$^1$H NMR (400 MHz, CDCl$_3$): 9.92 (1H, d, $J$ = 1.2 Hz), 7.87-7.86 (1H, m), 7.82 (1H, d, $J$ = 4.0 Hz), 7.54-7.51 (2H, m), 7.38-7.35 (3H, m) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): 182.59, 143.56, 138.44, 137.07, 131.63, 128.78, 128.48, 123.94, 122.43, 90.01, 82.77 ppm. IR (CH$_2$Cl$_2$): (C=O) 1675 cm$^{-1}$, (C=C) 2214 cm$^{-1}$. m.p.: 128 – 129 ºC.
4-Bromo thiophene-2-carboxaldehyde (2.6 mmol, 500 mg), bis(triphenylphosphine) palladium(II) chloride (0.16 mmol, 112 mg, 6 %), triphenylphosphine (0.31 mmol, 81 mg, 12 %), cuprous iodide (0.16 mmol, 30 mg, 6 %) and 2-ethynylthiophene (3.27 mmol, 0.35 ml) were used. The crude product was purified by column chromatography using silica gel and CH$_2$Cl$_2$: hexane (50:50) as mobile phase which afforded a bright yellow solid. Yield: 471 mg, 2.16 mmol, 83 %.

$^1$H NMR (400 MHz, CDCl$_3$): 9.92 (1H, d, $J = 1.2$ Hz), 7.86-7.85 (1H, m), 7.83-7.82 (1H, m), 7.33-7.32 (1H, m), 7.30-7.29 (1H, m), 7.03-7.01 (1H, m) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): 182.54, 143.64, 138.19, 137.09, 132.50, 127.91, 127.24, 123.59, 86.44, 83.32 ppm. IR (CH$_2$Cl$_2$): (C=O) 1677 cm$^{-1}$, (C≡C) 2213 cm$^{-1}$. m.p.: 114 – 115 ºC.
2.3.3.1.6 4-(Thien-2-ylethynyl)benzaldehyde (NB-A6)

4-Bromo-benzaldehyde (3.0 mmol, 555 mg), bis(triphenylphosphine)palladium(II)chloride (0.18 mmol, 126 mg, 6 %), triphenylphosphine (0.36 mmol, 94 mg, 12%), cuprous iodide (0.18 mmol, 34 mg, 6 %) and 2-ethynylthiophene (3.0 mmol, 0.3 ml) were used. The crude product was purified by column chromatography on silica gel using CH₂Cl₂: petroleum Ether 40:60 (75:25) as mobile phase which afforded an orange yellow solid. Yield: 597 mg, 2.81 mmol, 94 %.

¹H NMR (400 MHz, CDCl₃): 10.02 (1H, s), 7.86 (2H, d, J = 8.4 Hz), 7.66 (2H, d, J = 8.4 Hz), 7.36-7.33 (2H, m), 7.05-7.03 (1H, m) ppm. ¹³C NMR (100 MHz, CDCl₃): 191.42, 135.42, 132.89, 131.81, 129.62, 129.26, 128.38, 127.35, 122.45, 92.27, 86.80 ppm. IR (CH₂Cl₂): (C=O) 1701 cm⁻¹, (C≡C) 2206 cm⁻¹. m.p.: 101 – 103 °C.
4-Bromobenzaldehyde (4.5 mmol, 833 mg), bis(triphenylphosphine)palladium(II)chloride (0.18 mmol, 126 mg, 6 %), triphenylphosphine (0.36 mmol, 94 mg, 12%), cuprous iodide (0.18 mmol, 34 mg, 6 %) and 3-ethynylthiophene (3.0 mmol, 0.29 ml) were used. The crude product was purified by column chromatography on silica gel using CH$_2$Cl$_2$ : petroleum ether 40:60 (75:25) as mobile phase which afforded an orange yellow solid. Yield: 522 mg, 2.46 mmol, 82 %.

$^1$H NMR (400 MHz, CDCl$_3$): 10.02 (1H, s), 7.86 (2H, d, $J = 8.4$ Hz), 7.66 (2H, d, $J = 8.4$ Hz), 7.60-7.59 (1H, m), 7.35-7.33 (1H, m), 7.23-7.22 (1H, m) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): 191.46, 135.35, 132.00, 129.81, 129.74, 129.61, 125.74, 121.60, 88.65, 88.16 ppm. IR (CH$_2$Cl$_2$): (C=O) 1703 cm$^{-1}$, (C≡C) 2207 cm$^{-1}$. m.p.: 129 – 134 ºC.
2.3.3.2 Procedure for the preparation of porphyrins via the Adler method

2.3.3.2.1 5,10,15,20-Tetraphenylporphyrin (H₂TPP)

Benzaldehyde (30 mmol, 3.05 ml) and pyrrole (30 mmol, 2.08 ml) were added to 100 ml propionic acid. The reaction mixture was brought to reflux temperature for 90 minutes and then allowed to cool and left overnight. The porphyrin was filtered off and repeatedly washed with cold methanol affording a purple crystalline solid. Yield: 920 mg, 1.49 mmol, 20%. Spectroscopic data were in good agreement with reported data.⁵⁶

¹H NMR (400 MHz, CDCl₃): 8.85 (8H, s), 8.23-8.21 (8H, m), 7.77-7.75 (12H, m), -2.86 (2H, s) ppm. ¹³C NMR (100 MHz, CDCl₃): 142.11, 134.52, 127.67, 126.65, 120.09 ppm.
The freebase porphyrins were prepared via a modified version of Lindsey’s two-step one-flask room temperature reaction for the synthesis of meso-substituted porphyrins. Molar equivalents of pyrrole and the appropriate aldehyde were dissolved in 200 ml of dichloromethane and the solution was purged with argon for 10 minutes. For the thienyl porphyrins the reaction mixture was then cooled to 0 °C before the addition of the acid catalyst, BF$_3$·OEt$_2$ (0.1 equiv.). Cooling of the reaction mixture was not required for the tetraphenylporphyrins. The reaction mixture was allowed to stir overnight at room temperature. $p$-Chloranil (0.75 equiv.) was added to the solution and stirring continued for a further 6 hours [note: as $p$-chloranil is an oxidising agent the solution no longer needs to be kept under argon at this point.] The volume of solvent was then reduced to ca. 25 ml and the crude mixture was purified by column chromatography.
2.3.3.3.1 5,10,15,20-Tetra(thien-2-yl)porphyrin (H₂TThP)

Pyrrole (5 mmol, 0.35 ml), 2-thiophencarboxaldehyde (5 mmol, 0.47 ml), BF₃.OEt₂ (0.50 mmol, 63.36 µl) and p-chloranil (3.75 mmol, 922 mg) was used. The crude product was purified by column chromatography using silica gel and CH₂Cl₂ as mobile phase which afforded a greenish purple solid. Yield 145 mg, 0.23 mmol, 18 %. Spectroscopic data were in good agreement with the reported data.⁵⁶

¹H NMR (400 MHz, CDCl₃): 8.97 (8H, s), 7.85 (4H, dd, ³J = 3.2 Hz, ⁴J = 1.2 Hz), 7.78 (4H, dd, ³J = 5.2 Hz, ⁴J = 1.2 Hz), 7.44 (4H, dd, ³J = 5.2 Hz, ⁴J = 3.2 Hz), -2.72 (2H, s) ppm. ¹³C NMR (100 MHz, CDCl₃): 146.90, 142.62, 133.89, 127.90, 126.08, 112.38 ppm.
2.3.3.3.2 5,10,15,20-Tetra(5-(phenylethynyl)thien-2-yl)porphyrin (NB-H$_2$P1)

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\begin{align*}
\text{Pyrrole (3.53 mmol, 0.25 ml) and 5-(phenylethynyl)thiophene-2-carboxaldehyde (3.53 mmol, 750 mg), BF}_3\text{.OEt}_2 \ (0.35 \text{ mmol, 45 µl}) \text{ and } p\text{-chloranil (2.65 mmol, 645 mg) was used. The crude product was purified by column chromatography using silica gel and CH}_2\text{Cl}_2 : \text{petroleum ether 40:60 (80:20) as mobile phase which afforded a greenish purple solid. Yield: 257 mg, 0.25 mmol, 28 %}. \\
\end{align*}
\]

$^1$H NMR (600 MHz, CDCl$_3$): 9.15 (8H, s), 7.83 (4H, d, $J = 3.6$ Hz), 7.71 (4H, d, $J = 3.6$ Hz), 7.66-7.64 (8H, m), 7.43-7.39 (12H, m), -2.71 (2H, s) ppm. $^{13}$C NMR (150 MHz, CDCl$_3$): 143.10, 133.03, 131.52, 130.60, 130.25, 127.70, 127.47, 125.27, 121.81, 110.81, 93.42, 81.53 ppm.
2.3.3.3 5,10,15,20-Tetra(5-(thien-2-ylythynyl)thien-2-yl)porphyrin (NB-H$_2$P2)

Pyrrole (1.37 mmol, 95 µl) and 5-(thien-2-ylythynyl)thiophene-2-carboxaldehyde (1.37 mmol, 300 mg), BF$_3$.OEt$_2$ (0.14 mmol, 18 µl) and p-chloranil (1.03 mmol, 253 mg) was used. The crude product was purified by column chromatography using silica gel and CH$_2$Cl$_2$: petroleum ether 40:60 (80:20) as mobile phase which afforded a greenish purple solid. Yield: 83 mg, 0.08 mmol, 23%.

$^1$H NMR (600 MHz, CDCl$_3$): 9.12 (8H, s), 7.82 (4H, d, $J = 3.6$ Hz), 7.79 (4H, d, $J = 3.6$ Hz), 7.70-7.69 (4H, m), 7.41-7.37 (4H, m), 7.10-7.06 (4H, m) -2.65 (2H, s) ppm. $^{13}$C NMR (150 MHz, CDCl$_3$): 143.51, 133.09, 131.47, 130.43, 126.96, 126.32, 124.82, 121.86, 110.70, 86.68, 85.12. ppm.
2.3.3.3.4 5,10,15,20-Tetra(5-(thien-3-ylethynyl)thien-2-yl)porphyrin (NB-H$_2$P3)

Pyrrrole (1.37 mmol, 95 µl) and 5-(thien-3-ylethynyl)thiophene-2-carboxaldehyde (1.37 mmol, 300 mg), BF$_3$.OEt$_2$ (0.14 mmol, 18 µl) and $p$-chloranil (1.03 mmol, 253 mg) was used. The crude product was purified by column chromatography using silica gel and CH$_2$Cl$_2$ : petroleum ether 40:60 (80:20) as mobile phase which afforded a greenish purple solid. Yield: 61 mg, 0.06 mmol, 17 %.

$^1$H NMR (600 MHz, CDCl$_3$): 9.13 (8H, s), 7.82 (4H, d, $J = 3.6$ Hz), 7.70 (4H, d, $J = 3.6$ Hz), 7.67-7.66 (4H, m), 7.38-7.37 (4H, m), 7.36-7.31 (4H, m) -2.63 (2H, s) ppm. $^{13}$C NMR (150 MHz, CDCl$_3$): 142.96, 132.96, 130.21, 128.83, 128.24, 125.17, 124.93, 124.70, 120.92, 117.81, 110.80, 88.68, 80.93 ppm.
Pyrrole (2.0 mmol, 0.14 ml) and 4-(phenylethynyl)thiophene-2-carboxaldehyde (2.0 mmol, 424 mg), BF$_3$OEt$_2$ (0.2 mmol, 25 µl) and $p$-chloranil (1.5 mmol, 369 mg) was used. The crude product was purified by column chromatography using silica gel and CH$_2$Cl$_2$ : Et$_3$N (99:1) as mobile phase which afforded a greenish purple solid. Yield 135 mg, 0.13 mmol, 26%.

$^1$H NMR (600 MHz, CDCl$_3$): 9.12 (8H, s), 8.05 (4H, d, $J = 1.2$ Hz), 8.03 (4H, d, $J = 1.2$ Hz), 7.64-7.62 (8H, m), 7.41-7.38 (12H, m), -2.69 (2H, s) ppm. $^{13}$C NMR (150 MHz, CDCl$_3$): 141.75, 134.98, 131.19, 130.63, 130.31, 127.49, 126.52, 126.20, 122.17, 120.10, 110.46, 87.35, 81.39 ppm.
2.3.3.6  5,10,15,20-Tetra(4-(thien-2-ylethynyl)thien-2-yl)porphyrin (NB-H$_2$P$_5$)

Pyrrole (1.65 mmol, 0.11 ml) and 4-(thien-2-yethylthynyl)thiophene-2-carboxaldehyde (1.65 mmol, 360 mg), BF$_3$OEt$_2$ (0.17 mmol, 21 µl) and p-chloranil (1.24 mmol, 304 mg) was used. The crude product was purified by column chromatography using silica gel and CH$_2$Cl$_2$ : Et$_3$N (99:1) as mobile phase which afforded a greenish purple solid. Yield: 61 mg, 0.06 mol, 14 %.

$^1$H NMR (600 MHz, CDCl$_3$): 9.12 (8H, s), 8.07 (4H, d, $J$ = 1.2 Hz), 8.03 (4H, d, $J$ = 1.2 Hz), 7.40 (4H, d, $J$ = 3.6 Hz), 7.14 (4H, d, $J$ = 3.6 Hz), 7.09 – 7.06 (4H, m), -2.64 (2H, s) ppm. $^{13}$C NMR (150 MHz, CDCl$_3$): 141.67, 134.85, 131.13, 130.33, 126.40, 126.12, 122.27, 120.11, 110.49, 105.45, 87.42, 81.41 ppm.
2.3.3.7  5,10,15,20-Tetra(4-(thien-2-ylethynyl)phenyl)porphyrin (NB-H$_2$P6)

Pyrrole (1.44 mmol, 0.1 ml) and 4-(thien-2-ylethynyl)benzaldehyde (1.41 mmol, 300 mg), BF$_3$.OEt$_2$ (0.14 mmol, 18 µl) and p-chloranil (1.06 mmol, 260 mg) was used. The crude product was purified by column chromatography using silica gel and CH$_2$Cl$_2$:Et$_3$N (99:1) as mobile phase which afforded a greenish purple solid. Yield 40 mg, 0.04 mol, 11%.

$^1$H NMR (600 MHz, CDCl$_3$): 8.88 (8H, s), 8.21 (8H, d, $J = 8.4$ Hz), 7.92 (8H, d, $J = 8.4$ Hz), 7.44-7.42 (4H, m), 7.39-7.37 (4H, m), 7.11-7.09 (4H, m), -2.78 (2H, s) ppm. $^{13}$C NMR (150 MHz, CDCl$_3$): 144.93, 133.58, 131.20, 128.85, 126.57, 126.25, 122.31, 121.59, 118.66, 82.89, 81.33 ppm
2.3.3.8  5,10,15,20-Tetra(4-(thien-3-ylethynyl)phenyl)porphyrin (NB-H$_2$P7)

Pyrrrole (1.44 mmol, 0.1 ml) and 4-(thien-3-ylethynyl)benzaldehyde (1.41 mmol, 300 mg), BF$_3$·OEt$_2$ (0.14 mmol, 18 µl) and $p$-chloranil (1.06 mmol, 260 mg) was used. The crude product was purified by column chromatography using silica gel and CH$_2$Cl$_2$:Et$_3$N (99:1) as mobile phase which afforded a greenish purple solid. Yield: 59 mg, 0.06 mmol, 16 %.

$^1$H NMR (600 MHz, CDCl$_3$): 8.88 (8H, s), 8.20 (8H, d, $J = 8.4$ Hz), 7.92 (8H, d, $J = 8.4$ Hz), 7.68-7.67 (4H, m), 7.40-7.38 (4H, m), 7.35-7.34 (4H, m), -2.78 (2H, s) ppm. $^{13}$C NMR (150 MHz, CDCl$_3$): 141.73, 138.57, 134.35, 129.77, 129.71, 128.72, 127.65, 125.32, 115.81, 86.70, 81.53 ppm.
2.3.3.4  General procedure for metallation of porphyrins

The appropriate porphyrin was dissolved in ca. 20 ml CH$_2$Cl$_2$ and the solution was purged with argon for 10 minutes. 1.5 equivalents of Zn(OAc)$_2$ was first dissolved in ca. 5 ml MeOH and then added to the porphyrin solution. The reaction mixture was allowed to stir for ca. 10 hours. All solvents were removed under reduced pressure leaving a purple solid. This solid was dissolved in CH$_2$Cl$_2$ and washed successively with 5 % aqueous NaHCO$_3$, followed by water. The organic layer was dried over MgSO$_4$ and the solvent removed under reduced pressure. The metalloporphyrins were purified by column chromatography using silica gel and CH$_2$Cl$_2$ (100 %) as mobile phase. All metalloporphyrins synthesised in this manner were typically obtained in > 95 % yield.

2.3.3.4.1  Zinc(II)-5,10,15,20-tetraphenylporphyrin (ZnTPP)

Spectroscopic data were in good agreement with reported data.$^{57}$

$^1$H NMR (400 MHz, CDCl$_3$): 8.87 (8H, s) 8.18-8.15 (8H, m), 7.72-7.64 (12H, m) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$): 150.16, 142.77, 134.39, 131.39, 127.45, 126.51, 121.09 ppm.
Zinc(II)-5,10,15,20-tetra(thien-2-yl)porphyrin (ZnTThP)

Spectroscopic data were in good agreement with reported data.23

$^1$H NMR (400 MHz, CDCl$_3$): 9.07 (8H, s) 7.84 (4H, dd, $^3J = 3.6$ Hz, $^4J = 1.2$ Hz), 7.77 (4H, dd, $^3J = 3.6$ Hz, $^3J = 5.2$ Hz), 7.44 (4H, dd, $^3J = 3.6$ Hz, $^4J = 1.2$ Hz) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): 151.34, 143.00, 133.53, 132.15, 127.45, 125.94, 115.93, 113.17 ppm.
2.3.3.4.3 Zinc(II)-5,10,15,20-tetra(5-(phenylethynyl)thien-2-yl)porphyrin (NB-ZnP1)

\[
\begin{align*}
\text{R} &= \text{S} - \equiv - \text{C} \\
\text{Zn} &\quad \text{N} \quad \text{N} \\
\text{N} &\quad \text{N} \\
\text{R} &\quad \text{R} \\
\text{R} &\quad \text{R}
\end{align*}
\]

\(^1\text{H NMR}\) (400 MHz, CDCl\textsubscript{3}): 9.21 (8H, s), 7.79 (4H, d, \(J = 3.6\) Hz), 7.68 (4H, d, \(J = 3.6\) Hz), 7.51-7.49 (8H, m), 7.34-7.32 (12H, m) ppm. \(^{13}\text{C NMR}\) (100 MHz, CDCl\textsubscript{3}): 150.12, 144.02, 132.59, 131.24, 130.52, 130.13, 127.55, 127.43, 124.59, 121.88, 111.37, 87.28, 84.49 ppm. \textbf{Mass. Spec.} (MALDI): calculated 1102.69, observed 1102.5.
2.3.3.4 Zinc(II)-5,10,15,20-tetra(5-(thien-2-ylethynyl)thien-2-yl)porphyrin (NB-ZnP2)

![Chemical Structure](image)

**$^1$H NMR** (600 MHz, CDCl$_3$): 9.21 (8H, s), 7.80 (4H, d, $J = 3.0$ Hz), 7.69 (4H, d, $J = 3.0$ Hz, 7.41-7.40 (4H, m), 7.37-7.36 (4H, m), 7.08-7.07 (4H, m) ppm. **$^{13}$C NMR** (150 MHz, CDCl$_3$): 150.11, 144.37, 132.65, 131.39, 130.29, 126.83, 126.24, 124.14, 121.86, 111.32, 86.27, 85.26 ppm. **Mass Spec.** (MALDI): calculated 1126.8, observed 1126.1.
2.3.3.4.5 Zinc(II)-5,10,15,20-tetra(5-(thien-3-ylethynyl)thien-2-yl)porphyrin (NB-ZnP3)

![Chemical structure of Zinc(II)-5,10,15,20-tetra(5-(thien-3-ylethynyl)thien-2-yl)porphyrin](image)

$^1$H NMR (600MHz, CDCl$_3$): 9.22 (8H, s), 7.79 (4H, d, $J = 3$ Hz), 7.68 (4H, d, $J = 3$ Hz), 7.65-7.64 (4H, m), 7.37-7.36 (4H, m), 7.31-7.30 (4H, m) ppm. $^{13}$C NMR (150 MHz, CDCl$_3$): 150.21, 144.02, 132.70, 131.40, 130.10, 128.80, 128.23, 124.73, 121.06, 111.54, 88.42, 81.17 ppm. Mass Spec. (MALDI): calculated 1126.8, observed 1124.1.
2.3.3.4.6  Zinc(II)-5,10,15,20-tetra(4-(phenylethynyl)thien-2-yl)porphyrin
(NB-ZnP4)

\[
\text{R} = \begin{array}{c}
\text{S} \\
\text{R} \\
\text{R} \\
\text{Zn} \\
\text{R} \\
\text{R} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{N}
\end{array}
\]

\[\text{R} = \begin{array}{c}
\text{S} \\
\text{R} \\
\text{R} \\
\text{Zn} \\
\text{R} \\
\text{R} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{N}
\end{array} \]

\[^1H\text{ NMR} (600\text{ MHz, CDCl}_3): 9.13 (8H, s), 8.06 (4H, d, } J = 1.3 \text{ Hz), 8.05 (4H, d, } J = 1.3 \text{ Hz), 7.66-7.63 (8H, m), 7.42-7.38 (12H, m) ppm. } ^{13}\text{C NMR (150 MHz, CDCl}_3\text{): 150.22, 142.35, 139.57, 134.71, 131.35, 130.66, 129.73, 127.42, 122.10, 120.36, 111.33, 87.96, 84.02 ppm. Mass Spec. (MALDI): calculated 1102.69, observed 1102.5} \]
2.3.3.4.7 Zinc(II)-5,10,15,20-tetra(4-(thien-2-ylethynyl)thien-2-yl)porphyrin (NB-ZnP5)

\[
\begin{align*}
\text{R} & = \begin{array}{c}
\text{S} \\
\text{S} \\
\text{R} \\
\text{R} \\
\text{Zn} \\
\text{R} \\
\text{R}
\end{array} \\
\text{N} \\
\text{N}
\end{align*}
\]

$^1$H NMR (400 MHz, CDCl$_3$): 9.21 (8H, s), 8.04 (4H, d, $J = 1.2$ Hz), 8.02 (4H, d, $J = 1.2$ Hz), 7.37-7.36 (4H, m), 7.32-7.31 (4H, m), 7.05-7.03 (4H, m) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): 150.16, 142.27, 135.05, 133.20, 130.39, 126.45, 126.19, 122.38, 120.47, 111.26, 87.64, 83.99 ppm.
2.3.3.4.8 Zinc(II)-5,10,15,20-tetra(4-(thien-2-ylethynyl)phenyl)porphyrin (NB-ZnP6)

\[
\text{R} = \begin{array}{c}
\text{R} \\
\text{Zn} \\
\text{R} \\
\text{R} \\
\text{R}
\end{array}
\begin{array}{c}
\text{N} \\
\text{N} \\
\text{R} \\
\text{R} \\
\text{R}
\end{array}
\begin{array}{c}
\text{N} \\
\text{N} \\
\text{S}
\end{array}
\]

\[^{1}H\text{ NMR}\ (400\text{ MHz, CDCl}_3):\ 8.98\ (8\text{H, s}),\ 8.23\ (8\text{H, d, } J = 8.4\text{ Hz}),\ 7.93\ (8\text{H, d, } J = 8.4\text{ Hz}),\ 7.47-7.44\ (4\text{H, m}),\ 7.40-7.39\ (4\text{H, m}),\ 7.19-7.15\ (4\text{H, m})\ ppm.\ ^{13}C\text{ NMR}\ (100\text{ MHz, CDCl}_3):\ 150.07,\ 145.87,\ 133.28,\ 131.04,\ 129.05,\ 126.03,\ 121.63,\ 121.63,\ 121.51,\ 119.97,\ 82.79,\ 81.13\ ppm.\ \text{Mass. Spec. (MALDI): calculated 1102.69, observed 1101.7}
2.3.3.4.9 Zinc(II)-5,10,15,20-tetra(4-(thien-3-ylethynyl)phenyl)porphyrin (NB-ZnP7)

\[
\begin{align*}
R = \begin{array}{c}
\text{phenyl} \\
\text{thienyl}
\end{array}
\end{align*}
\]

\[^{1}H\text{ NMR}\ (600\ MHz, CDCl}_{3}\): 8.98 (8H, s), 8.23 (8H, d \(J = 8.4\ Hz\)), 7.93 (8H, d, \(J = 8.4Hz\)), 7.69-7.68 (4H, m), 7.42-7.39 (4H, m), 7.35-7.34 (4H, m) ppm. \[^{13}C\text{ NMR}\ (150\ MHz, CDCl}_{3}\): 150.49, 141.41, 139.28, 134.55, 129.62, 129.57, 128.79, 127.43, 125.15, 116.04, 85.88, 81.19 ppm. \textbf{Mass. Spec. (MALDI)}: calculated 1102.69, observed 1102.6
2.4 Results

2.4.1 UV-vis absorbance studies

A UV-vis spectrum typical of the porphyrins discussed in this chapter is displayed in figure 41. The electronic absorbance spectral features (\(\lambda_{\text{max}}\) for Soret and Q bands) of porphyrins synthesised in this study in addition to the extinction coefficients are listed in table 10. The absorbance spectra of ZnTPP and ZnTThP have been previously reported in the literature.\(^5\) The solvatochromic effect for NB-ZnP1 was studied in a range of solvents with the differences in absorbance \(\lambda_{\text{max}}\) of the Soret and Q bands listed in table 11.

![Figure 41](image)

*Figure 41*  Electronic absorbance spectrum of ZnTPP (insert Q bands region) recorded in CH\(_2\)Cl\(_2\).*
<table>
<thead>
<tr>
<th>Porphyrin</th>
<th>Soret (nm)</th>
<th>FWHM (cm(^{-1}))</th>
<th>Q bands (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnTPP</td>
<td>419 (2.53)(^a)</td>
<td>514</td>
<td>547 (9.72)(^c)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>588 (1.90)(^c)</td>
</tr>
<tr>
<td>ZnTThP</td>
<td>429 (2.84)(^a)</td>
<td>813</td>
<td>556 (9.48)(^c)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>600 (1.97)(^c)</td>
</tr>
<tr>
<td>NB-ZnP1</td>
<td>439 (2.75)(^a)</td>
<td>1197</td>
<td>559 (1.94)(^b)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>603 (6.40)(^c)</td>
</tr>
<tr>
<td>NB-ZnP2</td>
<td>439 (2.04)(^a)</td>
<td>1350</td>
<td>559 (1.42)(^b)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>603 (5.05)(^c)</td>
</tr>
<tr>
<td>NB-ZnP3</td>
<td>439 (1.81)(^a)</td>
<td>1252</td>
<td>559 (1.41)(^b)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>603 (4.95)(^c)</td>
</tr>
<tr>
<td>NB-ZnP4</td>
<td>429 (0.44)(^a)</td>
<td>870</td>
<td>555 (0.26)(^b)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>596 (0.45)(^c)</td>
</tr>
<tr>
<td>NB-ZnP5</td>
<td>425 (0.47)(^a)</td>
<td>828</td>
<td>550 (0.19)(^b)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>590 (0.85)(^c)</td>
</tr>
<tr>
<td>NB-ZnP6</td>
<td>426 (2.76)(^a)</td>
<td>772</td>
<td>550 (9.97)(^b)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>590 (2.30)(^c)</td>
</tr>
<tr>
<td>NB-ZnP7</td>
<td>425 (2.69)(^a)</td>
<td>775</td>
<td>550 (9.91)(^b)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>590 (2.25)(^c)</td>
</tr>
</tbody>
</table>

Table 10  UV-vis absorbance data of porphyrins recorded in CH\(_2\)Cl\(_2\).  \(^a\) Values in brackets refer to \(\varepsilon (x 10^5 \text{ M}^{-1} \text{ cm}^{-1})\).  \(^b\) Values in brackets refer to \(\varepsilon (x 10^4 \text{ M}^{-1} \text{ cm}^{-1})\).  \(^c\) Values in brackets refer to \(\varepsilon (x 10^3 \text{ M}^{-1} \text{ cm}^{-1})\).

<table>
<thead>
<tr>
<th>Porphyrin</th>
<th>Soret (nm)</th>
<th>FWHM (cm(^{-1}))</th>
<th>Q bands (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>439</td>
<td>1197</td>
<td>559, 602</td>
</tr>
<tr>
<td>Chloroform</td>
<td>442</td>
<td>1073</td>
<td>563, 607</td>
</tr>
<tr>
<td>DMSO</td>
<td>445</td>
<td>1059</td>
<td>570, 614</td>
</tr>
</tbody>
</table>

Table 11  Solvatochromic behaviour of NB-ZnP1 in different solvents.
The Soret band of ZnTPP and ZnTThP were observed at 419 and 429 nm respectively. Tetra(thien-2-yl)porphyrins, NB-ZnP1, NB-ZnP2 and NB-ZnP3 were red shifted and displayed their Soret band at 439 nm (Fig. 42). This was a bathochromic shift of 20 nm when compared to ZnTPP and 10 nm with respect to ZnTThP. Porphyrins, NB-ZnP4 and NB-ZnP5, with meso thien-2-yl units substituted at the thien-4-yl position were also shifted compared to ZnTPP, with both porphyrins displaying a $\lambda_{\text{max}}$ at lower energy than ZnTPP. The Soret band of NB-ZnP4 was observed at 429 nm, while for NB-ZnP5 the Soret $\lambda_{\text{max}}$ was at 425 nm. Both the porphyrins showed little or no change in their Soret band position with respect to ZnTThP ($\lambda_{\text{max}} = 429$ nm). They were however blue shifted when compared to the Soret bands of NB-ZnP1 – NB-ZnP3. Brückner et al. observed that substitution of the meso thien-2-yl ring at the thien-5-yl position caused a red shift in the porphyrins Soret absorbance band while substitution at the thien-3-yl position caused a minor blue shift. The tetra(phenyl)porphyrins, NB-ZnP6 and NB-ZnP7, undergo modest shifts. Both their Soret band $\lambda_{\text{max}}$, observed at 426 nm, were red shifted (7 nm bathochromic shift) with respect to the related porphyrin, ZnTPP.

For porphyrins NB-ZnP4 - NB-ZnP7, where small shifts were observed in the Soret band position, only minor changes were observed in the FWHM values (Table 10). However as the Soret band was shifted to lower energy for porphyrins NB-ZnP1, NB-ZnP2 and NB-ZnP3 the FWHM increases (FWHM: 1197, 1350 and 1252 cm$^{-1}$ respectively). This suggested increased electronic and vibronic coupling between the $\pi$-systems of the porphyrin ring and the meso pendant arms. Also an increase in the relative intensity of the Q(0,0) band can be observed as the electronic communication between the porphyrin and thienyl moieties increased. The ratio of the intensity of Q(0,0)/Q(1,0) bands (Fig. 43) increased significantly, with respect to ZnTPP and ZnTThP, for NB-ZnP1, NB-ZnP2, NB-ZnP3, NB-ZnP5 and NB-ZnP6. Thus the relative energies ground state and first excited singlet state were altered by appropriate substitution.
Figure 42  UV-vis spectra of ZnTPP, ZnTThP and NB-ZnP1 – NB-ZnP7 in CH$_2$Cl$_2$ at room temperature. All spectra have been normalised at their $\lambda_{\text{max}}$.

Figure 43  UV-vis spectra of Q band region of ZnTPP, ZnTThP and NB-ZnP1 – NB-ZnP7 recorded in CH$_2$Cl$_2$ at room temperature. All spectra have been normalised at their $\lambda_{\text{max}}$. 
2.4.2 Steady – state fluorescence studies

Fluorescence spectra were obtained for the thienyl and phenyl substituted porphyrins produced and compared to ZnTPP and ZnTThP. Table 12 below presents the emission maxima of the Q bands of the porphyrins and their respective singlet lifetimes, while table 13 illustrates the solvatochromic effects induced in a range of solvents.

<table>
<thead>
<tr>
<th>Porphyrin</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>Stokes shift (cm$^{-1}$)</th>
<th>$^1\tau$ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnTPP</td>
<td>595, 643</td>
<td>200</td>
<td>1.83</td>
</tr>
<tr>
<td>ZnTThP</td>
<td>617, 658</td>
<td>459</td>
<td>1.41</td>
</tr>
<tr>
<td>NB-ZnP1</td>
<td>634</td>
<td>811</td>
<td>0.80</td>
</tr>
<tr>
<td>NB-ZnP2</td>
<td>635</td>
<td>836</td>
<td>0.72</td>
</tr>
<tr>
<td>NB-ZnP3</td>
<td>635</td>
<td>836</td>
<td>0.72</td>
</tr>
<tr>
<td>NB-ZnP4</td>
<td>613, 652</td>
<td>465</td>
<td>0.83</td>
</tr>
<tr>
<td>NB-ZnP5</td>
<td>601, 647</td>
<td>310</td>
<td>1.39</td>
</tr>
<tr>
<td>NB-ZnP6</td>
<td>605, 646</td>
<td>420</td>
<td>1.77</td>
</tr>
<tr>
<td>NB-ZnP7</td>
<td>603, 650</td>
<td>365</td>
<td>1.47</td>
</tr>
</tbody>
</table>

Table 12 Fluorescence maxima and singlet lifetimes ($^1\tau$) of ZnTPP, ZnTThP and tetra aryl porphyrins studied, all recorded in CH$_2$Cl$_2$ at room temperature. Singlet lifetimes (+/- 0.03 ns)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>Stokes shift (cm$^{-1}$)$^a$</th>
<th>$^1\tau$ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>634</td>
<td>838</td>
<td>0.94</td>
</tr>
<tr>
<td>Chloroform</td>
<td>638</td>
<td>801</td>
<td>0.91</td>
</tr>
<tr>
<td>DMSO</td>
<td>640</td>
<td>662</td>
<td>0.82</td>
</tr>
</tbody>
</table>

Table 13 Fluorescence maxima and singlet lifetimes ($^1\tau$) of NB-ZnP1 recorded in chloroform, toluene and DMSO.
The fluorescence spectra of \textit{ZnTPP}, \textit{ZnTThP} and the novel porphyrins studied are shown below (Fig. 44 and 45). The first striking difference in the fluorescence spectra of \textit{meso} tetra(thien-2-yl)porphyrins \textit{NB-ZnP1}, \textit{NB-ZnP2} and \textit{NB-ZnP3} was that the emission bands which arise from the Q(0,0)* and Q(1,0)* excited states were totally unresolved due to the large red shift of the higher energy of the Q(0,0)* state, with the Q(1,0)* emission band stretching out to longer wavelengths (Fig. 44). \textit{NB-ZnP4} retained the emission profile similar to \textit{ZnTThP}, \textit{albeit} with a slight increase in the intensity of its bands, while the fluorescence emission profile of \textit{NB-ZnP5} was significantly increased in intensity and was hypsochromically shifted (the Q(0,0)* band underwent a 12 nm blue shift, Q(1,0)* band underwent a 5 nm blue shift). The fluorescence spectra observed for \textit{NB-ZnP6} and \textit{NB-ZnP7} although similar to that of \textit{ZnTPP}, were red shifted. The intensity of the bands was generally higher than that of \textit{ZnTPP} and also the Q(0,0)* band was more intense than the Q(1,0)*.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fluorescence_spectra.png}
\caption{Fluorescence spectra of \textit{ZnTPP}, \textit{ZnTThP} and \textit{NB-ZnP1} – \textit{NB-ZnP3}. All spectra were recorded in CH$_2$Cl$_2$ at room temperature ($\lambda_{exc} = 555$ nm, abs = 0.2 at 555 nm).}
\end{figure}
Figure 45 Fluorescence spectra of ZnTPP, ZnTThP and NB-ZnP4 – NB-ZnP7. All spectra were recorded in CH$_2$Cl$_2$ at room temperature ($\lambda_{exc} = 555$ nm, abs = 0.2 at 555 nm).

The fluorescence lifetimes (\(\tau\)) were recorded in dichloromethane and are included in table 12. A lifetime of 1.83 ns was observed for ZnTPP, which is in good agreement with the literature reported value of 2.0 ns. All porphyrins studied showed reduced fluorescence lifetimes relative to ZnTPP. The tetra(thein-2-yl)porphyrins studied showed a substantial decrease in lifetimes which ranged from 0.72 to 1.39 ns. The shortest lifetime observed in the series was that of NB-ZnP2 and NB-ZnP3 (0.72 ns). In keeping with its increased emission intensity NB-ZnP5 possessed the longest lifetime in the thien-2-yl series (1.39 ns). The lifetime of both tetra(phenyl)porphyrins, NB-ZnP6 and NB-ZnP7, was reduced to 1.56 and 1.47 ns respectively compared to ZnTPP. Typical fluorescence decays observed for NB-ZnP1 and NB-ZnP6 are shown in figure 46 and 47.
Figure 46  Typical fluorescence decay observed for **NB-ZnP1** (\(\tau = 0.80\) ns) at 633 nm, following excitation at 630 nm. Singlet lifetime (+/- 0.03 ns).

Figure 47  Typical fluorescence decay observed for **NB-ZnP6** (\(\tau = 1.77\) ns) at 603 nm, following excitation at 630 nm. Singlet lifetimes (+/- 0.03 ns).
2.4.3 Laser flash photolysis studies

Transient absorbance measurements following laser flash photolysis, at 355 and 532 nm, were carried out in toluene under one atmosphere of argon at room temperature with a typical sample absorbance of 0.08 (± 0.02) AU. All transient species were formed within the lifetime of the laser pulse (ca. 10 ns) and were independent of excitation wavelength. The transient absorbance spectrum of each porphyrin was obtained between 350 and 600 nm. All porphyrins studied gave rise to a transient signal with a maximum in the region 440 – 500 nm. A typical transient decay observed following flash photolysis of ZnTPP at 532 nm excitation is shown in figure 48. The transient species is ascribed to the lowest energy \( ^3(\pi-\pi^*) \) triplet excited state of the porphyrin complex. A depletion was also observed in the Soret region of the spectrum attributed to the depletion of the porphyrin ground state. The lifetimes of the triplet excited state are given in table 14. Table 15 gives the results of a solvatochromic study of NB-ZnP1.

<table>
<thead>
<tr>
<th>Porphyrin</th>
<th>( ^3\tau ) (μs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnTPP</td>
<td>24</td>
</tr>
<tr>
<td>ZnTThP</td>
<td>20</td>
</tr>
<tr>
<td>NB-ZnP1</td>
<td>9</td>
</tr>
<tr>
<td>NB-ZnP2</td>
<td>7</td>
</tr>
<tr>
<td>NB-ZnP3</td>
<td>11</td>
</tr>
<tr>
<td>NB-ZnP4</td>
<td>36</td>
</tr>
<tr>
<td>NB-ZnP5</td>
<td>51</td>
</tr>
<tr>
<td>NB-ZnP6</td>
<td>26</td>
</tr>
<tr>
<td>NB-ZnP7</td>
<td>54</td>
</tr>
</tbody>
</table>

*Table 14* Triplet lifetimes of porphyrins recorded in toluene at 1 atm argon. Triplet lifetimes (+/- 10 %) μs.
<table>
<thead>
<tr>
<th>Solvent</th>
<th>$^3\tau$ (µs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>9</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>8</td>
</tr>
<tr>
<td>Ethyl Acetate</td>
<td>7</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>7</td>
</tr>
<tr>
<td>Dimethyl Sulfoxide</td>
<td>7</td>
</tr>
</tbody>
</table>

Table 15  
Triplet lifetimes of NB-ZnP1 recorded in various solvents at 1 atm argon.  
Triplet lifetimes (+/- 10 %) µs.

![Transient spectrum of ZnTPP in toluene following 532 nm excitation under 1 atm of argon.](image)

Figure 48  
Transient spectrum of ZnTPP in toluene following 532 nm excitation under 1 atm of argon.

The excited state transient absorbance difference spectrum of ZnTPP was characterised by a weak absorbance from 300 to 390 nm in the ultraviolet region and a strong absorbance from 435 to 540 nm in the visible with a $\lambda_{\text{max}}$ at 470 nm. A depletion observed between 400 and 435 nm which equated to the Soret band absorbance of the parent species. Isobestic points were present at 400, 435 and 538 nm indicating that the spectral changes were caused by a clean conversion between two states. At longer wavelengths only weak absorbances were observed.18
The excited state transient absorbance difference spectra of ZnTThP was red shifted relative to ZnTPP where the $\lambda_{\text{max}}$ occurred at 490 nm. A depletion of the ground state was observed as a negative bleach centred at 430 nm. Weak absorbances were observed in the UV region from 300 – 390 nm with further weak absorbance detected in the region 550 – 600 nm.

The tetra(thien-2-yl)porphyrins, NB-ZnP1 – NB-ZnP5, also showed bathochromically shifted transient absorbance difference spectra with respect to ZnTPP. Similar to ZnTThP the $\lambda_{\text{max}}$ occurred between 450 and 520 nm. Lower energy absorbances that extended past 600 nm were also observed. The profile of the transient absorbance difference spectra and the lifetimes of the transient signals obtained were independent of excitation wavelength (Fig. 49 and 50). NB-ZnP6 and NB-ZnP7 possessed transient absorbance difference spectra very similar to that of ZnTPP with their $\lambda_{\text{max}}$ at 450 nm, weak absorbances in the UV region and no additional absorbances obvious at longer wavelength.

*Figure 49*  
*Transient absorbance difference spectra of NB-ZnP1 in toluene following 355 nm excitation under 1 atm argon.*
Figure 50  Transient absorbance difference spectra of NB-ZnP1 in toluene following 532 nm excitation under 1 atm argon.

Figure 51  Transient absorbance difference spectra of NB-ZnP2 in toluene following 355 nm excitation under 1 atm argon.
Figure 52  Transient absorbance difference spectra of NB-ZnP5 in toluene following 355 nm excitation under 1 atm argon.

Figure 53  Transient absorbance difference spectra of NB-ZnP7 in toluene following 355 nm excitation under 1 atm argon.
2.4.4 Electrochemistry

Porphyrrins are electroactive systems and undergo multiple redox processes. The cyclic voltammogram of ZnTThP is shown in figure 54. In general metalloporphyrins display one or two ring centred oxidations and one or two ring centred reductions. Substitution at the meso position of the porphyrin macrocycle had an effect on the electrochemistry of the porphyrin ring. The two $E_{1/2}$ values observed at positive potential (Table 16) correspond to the first and second reversible oxidations of the porphyrin $\pi$ system which result in the formation of the porphyrin cation radical and porphyrin dication radical respectively. Generally there were two reduction processes observed at negative potential corresponding to the formation of the porphyrin anion radical and dianion species.

![Cyclic voltammogram showing oxidation and reduction waves of ZnTThP in CH$_2$Cl$_2$](image)

Figure 54  Cyclic voltammogram showing oxidation and reduction waves of ZnTThP in CH$_2$Cl$_2$.\textsuperscript{5}
<table>
<thead>
<tr>
<th>Porphyrin</th>
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<th>Reduction</th>
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<tr>
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<td>2nd</td>
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<tr>
<td></td>
<td>$E_{1/2}$</td>
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</tr>
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<tr>
<td>NB-ZnP7</td>
<td>0.85</td>
<td>1.14</td>
</tr>
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</table>

*Table 16* Redox potentials of porphyrins recorded in CH$_2$Cl$_2$ reported vs. SCE.
Notably, all the *meso* tetrathein-2-yl porphyrins showed an anodic shift of their first oxidation relative to *ZnTPP*, which indicated a stabilisation of the HOMO orbital of the porphyrin. An anodic shift of 110, 120 and 130 mV was observed for *NB-ZnP1*, *NB-ZnP2* and *NB-ZnP3* respectively compared to *ZnTPP* (*E_{1/2} = +0.78 vs. SCE*). Porphyrins *NB-ZnP4* and *NB-ZnP5* displayed a smaller shift in their first oxidation potential to +0.85 and +0.86 V vs. SCE (70 and 80 mV anodic shift), compared to the first oxidation of *ZnTPP*. Thus the stabilisation of the HOMO orbital was less pronounced when the *meso* thienyl ring is substituted in the thien-4-yl position. The tetraphenyl substituted porphyrins (*NB-ZnP6* and *NB-ZnP7*) underwent a similar shift of their first oxidation, observed 80 and 70 mV anodic of *ZnTPP*.

Destabilisation of the LUMO orbitals also occurs with a decrease in the potential of the first reduction. Again *NB-ZnP1* – *NB-ZnP3* showed the largest effect with a decrease in their reduction potential compared to *ZnTPP*. The largest effect was observed for *NB-ZnP1* which displayed a reduction 250 mV anodic of *ZnTPP*. *NB-ZnP2* and *NB-ZnP3* showed their reduction at 240 and 150 mV anodic of *ZnTPP* respectively (*ZnTPP E_{1/2} = -1.41 vs. SCE*). Destabilisation of the LUMO is less pronounced for the remainder of the porphyrins examined. Both thienyl porphyrins *NB-ZnP4* and *NB-ZnP5* were shifted by 100 and 90 mV respectively (*E_{1/2} = -1.31 V and -1.32 V vs. SCE*). There was no evident shift in the first reduction of *NB-ZnP6* and only a slight cathodic shift for *NB-ZnP7* (*E_{1/2} = -1.43 V vs. SCE*).
Figure 55  Cyclic voltammogram of NB-ZnP2 showing oxidation and reduction waves.

Figure 56  Cyclic voltammogram of NB-ZnP3 showing oxidation and reduction waves.
Figure 57  Cyclic voltammogram of NB-ZnP5 showing oxidation and reduction waves.

Figure 58  Cyclic voltammogram of NB-ZnP7 showing oxidation and reduction waves.
2.5 Discussion

2.5.1 Synthesis and $^1$H NMR spectra

The porphyrins produced in this study were synthesised using standard conditions involving the condensation of pyrrole with 4/5-substituted thien-2-ylcarboxaldehydes and 4-substituted benzaldehydes. Initially $\text{H}_2\text{TPP}$ was synthesised via the Adler method, although synthesis of $\text{H}_2\text{TThP}$ by the same method proved problematic. This was ascribed to possible decomposition of the porphyrin under such harsh conditions, elevated temperature (141 ºC) and the acidic environment (propionic acid). Using a modified Lindsey procedure, $\text{H}_2\text{TThP}$ was produced in 18 % yield. It had previously been noted that addition of BF$_3$.OEt$_2$ to the reaction flask at 0 ºC improved the yields for thienyl porphyrins.$^{56}$ Thus this condition was employed for the synthesis of the meso tetra(thien-2-yl)porphyrins NB-ZnP1 – NB-ZnP5. The reduction in temperature was not required for the phenyl substituted porphyrins, NB-ZnP6 and NB-ZnP7. Metallation of all porphyrins using zinc acetate was carried out quantitatively. Melting points for all porphyrins were greater than 300 ºC.

Each of the porphyrins in this study are A$_4$-type meso-substituted porphyrins, which are of $S_4$ symmetry and possess a $C_4$ rotational axis through the metal centre perpendicular to the plane of the ring. As each of the β-pyrrolic protons is in an identical environment a sharp singlet is produced in the $^1$H NMR spectra. This singlet occurs at 8.87 ppm for ZnTPP however it is shifted depending on the substituents. Porphyrins NB-ZnP6 and NB-ZnP7 which have the phenyl ring attached directly to the porphyrin macrocycle and are substituted at the para position with ethynylthien-2-yl and ethynylthien-3-yl groups respectively, display β-pyrrolic signals at 8.89 ppm in the $^1$H NMR spectra. However the β-pyrrolic signal for meso tetra(thien-2-yl)porphyrin is shifted further downfield with ZnTThP displaying a signal at 9.07 ppm. For the (thien-2-yl)porphyrins in this study, NB-ZnP1 - NB-ZnP5, the β-pyrrolic signal is observed in the range 9.20 – 9.22 ppm. This deshielding effect of the β-pyrrolic protons observed for the meso thien-2-ylporphyrins has previously been observed and was ascribed to an increase in the ring current of the porphyrin ring caused by delocalisation onto the peripheral thienyl units.$^{5,9,25,27,60}$ The presence of a singlet in the region -2.5 to -2.8 ppm arises from the endocyclic protons at the centre of the porphyrin which are exclusive to the freebase
porphyrins. The internal protons experience this high field shift because of the internal ring current of the porphyrin macrocycle. The absence of this signal confirms the presence of a metal at the centre of the porphyrin ring. Figures 59 and 60 give an overlay of the aromatic region of the $^1$H NMR spectra for the tetra substituted porphyrins ZnTPP, ZnTThP, and various porphyrins studied, all recorded in CDCl$_3$. 
Figure 59  An overlay of the aromatic region of the $^1$H NMR spectra ($\delta$) for $H_2TPP$ (a), $NB-H_2P6$ (b) and $NB-H_2P7$ (c) in CDCl$_3$. 
Figure 60  An overlay of the aromatic region of the $^1$H NMR spectra ($\delta$) for ZnTThP (a), NB-ZnP1 (b), NB-ZnP3 (c) and NB-ZnP4 (d) in CDCl$_3$. 
2.5.2 UV-vis absorbance studies

Historically there have been mixed reports as to whether there exists electronic communication between the porphyrin macrocycle and thienyl substituents when attached via the meso-position.\textsuperscript{5,25,27,60} However in more recent publications, the influence of thienyl substituents on ground and excited state electronics has been observed and the source of these changes were examined using both theoretical and experimental methods.\textsuperscript{18,28} Direct substitution of the porphine core with aromatic thiophene moieties does lead to electronic interaction between the two $\pi$-systems. This can also be enhanced through appropriate substitution of the thienyl groups. The UV-vis spectra of NB-ZnP1 – NB-ZnP7, were shown in figure 42 and 43, are compared to ZnTPP and ZnTThP.

The UV-vis spectra of porphyrins, NB-ZnP1 – NB-ZnP3, were bathochromically shifted with respect to both ZnTPP and ZnTThP. These porphyrins also possess the highest FWHM values for the porphyrin Soret band of all porphyrins studied. Bathochromic shifts in the UV-vis spectra and increasing FWHM of the Soret band are evidence of increased coupling of the overlapping $\pi$ systems. Rochford et al. reported that appropriate substitution of the meso thienyl groups resulted in increased coupling of the $\pi$ systems.\textsuperscript{18} Therefore the changes observed for NB-ZnP1 – NB-ZnP3 may be due to enhanced delocalisation when substituents (ethynylbenzene, ethynyl-2-thiophene and ethynyl-3-thiophene respectively) were in the thien-5-yl position. Within this group changing the terminal aryl group attached to the meso thien-2-ylethynyl arms did not change the UV-vis spectra significantly. Although, the FWHM would suggest that the $\pi$ systems of NB-ZnP2, which has two thien-2-yl moieties are coupled more strongly.

The UV-is spectra of porphyrins NB-ZnP4 and NB-ZnP5 were red shifted with respect to both ZnTPP but not ZnTThP. The Soret and Q bands were equal to and hypsochromically shifted respectively when compared to ZnTThP. Also the FWHM values were very similar to ZnTThP. The conjugation is not effective when the ethynylbenzene and ethynyl-2-thiophene are in the thien-4-yl position. This suggests that the conjugation pathway that allows for greatest $\pi – \pi$ overlap occurred when the ethynylaryl substituents are in the distal position of the meso thien-2-yl ring.
Changes in the absorbance spectra of thien-2-yl porphyrins substituted with a methyl group were reported. When substituted at the thien-5-yl position, a red shift in the UV-vis spectrum was observed. While substitution with a methyl group in the thien-3-yl position caused a blue shift. The authors attributed this change in absorbance to the conformation the thienyl rings adopted. Thus substitution the thien-4-yl position may hinder the co-planar conformation of the thienyl rings with respect to the porphyrin macrocycle.

The UV-is spectra of porphyrins NB-ZnP6 and NB-ZnP7 were red shifted with respect to both ZnTPP. Substitution with ethynylthiophenes at the para position of the phenyl ring allowed for increased conjugation throughout the meso pendant arms. Studies on phenylacetylene building blocks have shown that para substituted phenylacetylene compounds possess greater conjugation of the π systems. Although the phenyl rings are not co-planar to the porphyrin macrocycle, porphyrins NB-ZnP6 and NB-ZnP7 were red shifted and display higher FHWM values than ZnTPP. This indicates that there is increased coupling of the π systems even though the meso substituents lie in an idealised orthogonal manner with respect to the porphyrin macrocycle.
2.5.3 Steady–state fluorescence studies

The fluorescence spectra of porphyrins, **NB-ZnP1** – **NB-ZnP3**, were also shifted to higher energy with respect to both **ZnTPP** and **ZnTThP**. The Q(0,0)* band was red shifted to a greater extent than the Q(1,0)* band, such that the individual emission bands were totally unresolved. The changes in lifetime within the group were quite small, although all were reduced with respect to **ZnTThP**. This is in agreement with literature, where substitution of thienyl rings caused a reduction in singlet lifetimes.27

Porphyrins **NB-ZnP4** and **NB-ZnP5** displayed quite interesting fluorescence spectra. **NB-ZnP4** displayed a fluorescence spectrum typical of thienyl porphyrins with two Q* bands but with emission intensity higher than that of **ZnTThP**. However, **NB-ZnP5** possessed an emission profile that was significantly different from **NB-ZnP4** and **ZnTThP**. The Q(0,0)* band was bathochromically shifted with respect to both and the intensity of the emission was much higher. The lifetime of **NB-ZnP4** was reduced with respect to **ZnTThP** by approximately 40 %, whereas the lifetime of **NB-ZnP5** not reduced (within instrumental error).

For the phenyl substituted porphyrins, **NB-ZnP6** and **NB-ZnP7**, a minor red shift in the Q(0,0)* and Q(1,0)* emission bands was observed together with an increase in the intensity of the Q(0,0)* band relative to **ZnTPP**. The emission spectra are the mirror image of the UV-vis spectra where a similar increase in the Q bands was observed. A reduction of fluorescence lifetimes, approximately 15 - 20 %, was also observed for the phenyl porphyrin analogues. Previously, a small reduction in fluorescence lifetime was noted for tetraphenylporphyrins when an additional phenylethynyl linker was placed between the porphyrin ring and the *meso* phenyl ring.63
2.5.4 Laser flash photolysis studies

The transient absorbance difference spectra were ascribed to the lowest $^3(\pi - \pi^*)$ porphyrin excited state. All transient signals recorded in this study fitted well with mono-exponential kinetics indicating unimolecular decay. Triplet lifetimes for ZnTPP and ZnTThP were previously reported as 24 and 20 µs respectively.$^{18}$ Triplet lifetimes reported throughout this study were (+/-) 10 % µs.

The transient absorbance difference spectra of the thienyl porphyrins, NB-ZnP1 – NB-ZnP5 were bathochromically shifted with respect to ZnTPP but in a similar range to ZnTThP. Low energy absorbances that extended past 600 nm were observed. These excited state characteristics suggested an increase in the electronic coupling of the porphyrin ring and the thienyl π-network upon excitation and possibly charge transfer onto the peripheral thien-2-yl π-system. These lower energy absorbance bands were not observed for the phenyl substituted porphyrins NB-ZnP6 and NB-ZnP7.

The lifetimes of the porphyrins varied widely with substitution pattern. Thienyl porphyrins substituted in the distal position, NB-ZnP1 – NB-ZnP3, were significantly reduced in comparison to both ZnTPP and ZnTThP. There was little change within the series as the terminal group was changed from benzene to 2-thiophene to 3-thiophene. Lifetimes were similar to those reported previously for substituted thien-2-ylethynyl porphyrins.$^{18}$

Upon further substitution of the meso thien-2-yl moieties at the thien-4-yl position, NB-ZnP4 and NB-ZnP5, significant changes in the triplet lifetimes were observed. The lifetime of the former was 36 µs and the latter, 51 µs. These are greatly increased compared to ZnTThP (20 µs). Also unexpected was the increase from NB-ZnP4 to NB-ZnP5 when only the terminal aryl group was changed.

The phenyl porphyrins NB-ZnP6 and NB-ZnP7 also showed some deviation from the norm. NB-ZnP6 possessed a lifetime similar to that of ZnTPP. This is not surprising given that both have a phenyl ring attached to the porphyrin macrocycle which lie orthogonal to each other. The lifetime of NB-ZnP7 is almost double that of the other phenyl porphyrins. As only the terminal aryl group has changed this is somewhat unusual.
2.5.5 NB-ZnP1 solvatochromism

Modest red shifts were observed in the UV-vis spectra for the Soret band $\lambda_{\text{max}}$ of NB-ZnP1 on going from toluene ($\lambda_{\text{max}} = 439$ nm) to chloroform ($\lambda_{\text{max}} = 442$ nm) to DMSO ($\lambda_{\text{max}} = 445$ nm) as can be seen in figure 61. Bathochromic shifts were also observed in the Q band region of the spectrum (Table 11).

The fluorescence spectra showed similar solvatochromic behaviour. As the Q(0,0)* emission band of NB-ZnP1 was red shifted to a greater extent than the Q(1,0)* band, a convergence of the bands occurred and the porphyrin fluorescence appeared as a single broad emission, nonetheless this emission band was red shifted on increasing solvent polarity from 634 nm in toluene to 638 nm in chloroform to 640 nm in DMSO.

![Figure 61](image-url)

*Figure 61* An overlay of the UV-vis absorbance and fluorescence emission spectra of NB-ZnP1 recorded in toluene (blue), chloroform (red) and DMSO (green). Absorbance spectra have been normalised at their $\lambda_{\text{max}}$. Emission spectra were recorded at room temperature ($\lambda_{\text{exc}} = 555$ nm, abs. $= 0.2$ at 555 nm).
The transient absorbance difference spectra of **NB-ZnP1** were recorded in various solvents of increasing polarity (ethyl acetate, acetonitrile and DMSO) between 450 and 800 nm following 532 nm excitation under 1 atm argon. In all solvents the spectral characteristics observed were similar to those discussed previously. The lifetime of the transient species were all within instrumental error (8 ± 1 µs, Table 15). However, a substantial increase in the lower energy absorbances was observed ranging from 580 nm to 800 nm (Fig. 62). This was possibly due to an excited state charge transfer transition. The transition gains oscillator strength on increasing the solvent polarity. The appearance of this low-energy band and the enhancement of the absorbance in polar media suggest that there was enhanced electronic communication between the porphyrin π-system and the *meso* thien-2-yl substituents on going from the ground state to the excited state of **NB-ZnP1**.

![Figure 62](image.png)  
*Figure 62  An overlay of transient absorbance difference spectra of **NB-ZnP1** in various solvents following 532 nm excitation under 1 atm argon. Each plot is taken 2 µs after the laser pulse.*
2.5.6 Influence of arylethynyl spacers on the photophysical properties of porphyrins

A study of arylethynyl spacer units at the meso position of porphyrin macrocycle was previously reported. The contribution of phenylethynyl spacers to the ground and excited singlet state was studied through changes in the absorbance and fluorescence spectra as well as fluorescence lifetime and fluorescence quantum yield. Figure 63 depicts a series 5,10,15,20-tetraarylporphyrins (A) and 5,10,15,20-(arylethynyl)phenyl porphyrins (B) reported in the literature.

\[
\begin{align*}
\text{Ar} & = \text{C}_6\text{H}_5 \\
4-\text{CH}_3\text{C}_6\text{H}_4 \\
4-\text{CF}_3\text{C}_6\text{H}_4 \\
4-\text{O}_2\text{NC}_6\text{H}_4 \\
3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3
\end{align*}
\]

*Figure 63* Series A, phenyl substituted porphyrins and series B, phenyl substituted porphyrins with an additional phenylethynyl spacer unit.

Comparison of the absorbance spectra of series A and series B showed only small differences in the $\lambda_{\text{max}}$ ($\pm$ 5 nm). From the absorbance spectra the authors concluded that the aryl substituents of A and 4-(arylethynyl)phenyl substituents of B were not strongly coupled to the porphyrin core. More distinct changes in the fluorescence properties were
observed when A and B were compared. The emission maxima were almost identical but the excited state lifetimes for porphyrins in series B were consistently shorter (3 – 15 %) than those observed for series A and fluorescence quantum yields were consistently higher for series B compared to A. The phenylethynyl spacer allowed minimal electronic communication between the porphyrin core and the aryl substituent in both the ground state and excited state (similarity of the absorbance and emission) which suggested the energy levels of the HOMO and LUMO were comparable for the series A and series B. However the contributions of a phenylethynyl spacer should be minimal as the electronic effects should were near identical when the aryl substituent itself was a phenyl ring.

When *meso* aryl groups are substituted with ethynyl units and further substituted with a second aryl moiety the influence on the ground state and excited state electronics may be perturbed. The direct contribution from (aryl)ethynyl spacers to the photophysics of the excited state have not been extensively examined for porphyrin systems. Figure 64 represent three series of porphyrins each with three varying (aryl)ethynyl spacers.
In this study, series 2 is examined. ZnTThP is the parent porphyrin and NB-ZnP2, NB-ZnP5 and NB-ZnP6, display three variations of arylethynyl spacer groups (Fig. 64). Substituents in the distal position of the thien-2-yl ring, as in NB-ZnP2, should possess the same steric requirements as ZnTThP, where the meso pendant arms lie in a co-planar arrangement with respect to the porphyrin macrocycle. It is possible that the substitution pattern on NB-ZnP5 may hinder the co-planar arrangement favoured by thien-2-yl groups. As noted earlier, the steric requirements for a five membered meso thienyl ring are smaller than that of a six membered meso phenyl ring. In the case of NB-ZnP6, the phenyl groups should lie in a low energy conformation, arranged in an idealised orthogonal fashion with respect to the mean plane of the porphyrin. Table 17 below presents the ground state and excited state data for the porphyrins.
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<th>Soret $\lambda_{\text{max}}$ (nm)</th>
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<th>Emission $\lambda_{\text{max}}$ (nm)</th>
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<td>26</td>
</tr>
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</table>

Table 17  Photophysical data of ZnTThP and (arylethynyl)thien-2-yl porphyrins, NB-ZnP2, NB-ZnP5 and NB-ZnP6.

Due to the contribution of conformations, in which the thienyl groups adopt idealised co-planar arrangements with the porphyrin ring, an efficient extension of the porphyrinic $\pi$-system through conjugation was observed. In the ground state this is signified as a red shift in the Soret band along with an increase in the FWHM value. This was the case for NB-ZnP2 which possessed the same steric requirements as ZnTThP but also possessed an extended $\pi$-framework. The minor hypsochromic shift observed in the Soret $\lambda_{\text{max}}$ of NB-ZnP5 was attributed to a somewhat encumbered rotational barrier due to substitution pattern and the orthogonal orientation of the phenyl ring in NB-ZnP6. The fluorescence lifetime of NB-ZnP5 (1.39 ns) was very close to that of ZnTThP (1.36 ns). However a reduction in singlet excited state lifetime was observed for NB-ZnP2 (0.72 ns) and NB-ZnP6 displayed an increase in fluorescence lifetime relative to ZnTThP.

A marked difference in triplet lifetime was also observed. The shortest triplet lifetime is that of NB-ZnP2 (7 µs), significantly reduced compared to ZnTThP (20 µs). The triplet lifetime of NB-ZnP6 (26 µs) is very similar to that of ZnTPP (24 µs) and ZnTThP (20 µs). Most interesting was NB-ZnP5 that had a triplet excited state lifetime of 51 µs. This increase in $^3(\pi-\pi^*)$ triplet lifetime was indicative of increased communication of the thienyl groups with the porphyrin $\pi$-network.
2.5.7 Electrochemistry

Electrochemical studies were performed on the porphyrins to elucidate the effect of substitution on the porphyrin macrocycle. The results showed that substitution of the porphyrin ring system at the *meso* position had an effect on its electrochemistry. All the porphyrins showed two one-electron oxidations and one, one-electron reduction.

Examination of the redox data (Table 16) revealed that the first oxidation potentials were shifted to more positive potential when the six membered *meso* phenyl moiety of ZnTPP was replaced with five membered *meso* thienyl groups (NB-ZnP1 – NB-ZnP5) indicating that the thienyl porphyrins are harder to oxidise than phenyl porphyrin. This stabilisation of the HOMO of the porphyrin macrocycle by the thienyl moiety was observed by Rochford et al.\(^{18}\) and more recently by Ghosh et al.\(^{64}\)

When the *meso* thien-2-yl moiety was substituted at the thien-5-yl position, the stabilisation was slightly higher. Higher oxidation potentials were observed for NB-ZnP1 – NB-ZnP3 compared to NB-ZnP4 and NB-ZnP5 which were substituted at the thien-4-yl position. Also the reduction potentials were shifted to less negative potentials for the thien-2-yl porphyrins NB-ZnP1 – NB-ZnP5. On replacement of the *meso* phenyl group with a thienyl moiety the LUMO was destabilised.

An increase in oxidation potentials was also observed for the phenyl porphyrins NB-ZnP6 and NB-ZnP7 relative to ZnTPP indicating stabilisation of the HOMO occurred. The reduction potentials were observed more negative than that of ZnTPP. This indicated that the LUMO is also stabilised. This result is interesting. Stabilisation of both the HOMO and LUMO would not be expected as the *meso* substituents are not co-planar to the porphyrin macrocycle and the \(\pi\) systems do not overlap. However stabilisation is brought to the macrocycle by the *meso* phenyl(ethynylthienyl) moieties.
2.6 Conclusions

Porphyrrins \(\text{NB-ZnP1 – NB-ZnP3}\) were synthesised with substituents at the thien-5-yl position, in order to examine whether an additional aryl group would cause further coupling of the overlapping \(\pi\) systems. The results showed that it did in fact cause increased coupling with bathochromic shift in the absorbance spectra and an increase in the FWHM values of the Soret band. No additional effect was observed in relation to the choice of terminal aryl ring. The singlet lifetime of the porphyrins were reduced relative to \(\text{ZnTTThP}\) as were the triplet lifetimes. Electrochemical analysis showed that extension of the conjugation on the \(meso\) thien-2-yl arms caused a stabilisation of the HOMO but destabilisation of the LUMO.

Porphyrrins \(\text{NB-ZnP4 and NB-ZnP5}\) possessed the same terminal substituents (ethynylbenzene and ethynylthien-2-yl) as \(\text{NB-ZnP1 and NB-ZnP2}\); however they are substituted at the thien-4-yl position. The conjugation of the \(meso\) substituents was not as effective in \(\text{NB-ZnP4 and NB-ZnP5}\). The absorbance spectra were generally unchanged when compared to \(\text{ZnTTThP}\). Both the singlet and triplet lifetimes were substantially changed. The singlet lifetimes were reduced compared to \(\text{ZnTTThP}\) but to a lesser extent than that observed for \(\text{NB-ZnP1 – NB-ZnP3}\). However the triplet lifetimes were significantly increased. This would suggest that the conformation of the thien-2-yl substituents with respect to the porphyrin macrocycle is changed when the \(meso\) thienyl ring is substituted at the thien-4-yl position and that caused the increase in lifetime as opposed to conjugation within the \(meso\) substituents.

Porphyrrins \(\text{NB-ZnP6 and NB-ZnP7}\) are phenyl substituted porphyrins which have been further substituted at the \(para\) position with ethynylthien-2-yl and ethynylthien-3-yl moieties respectively. These porphyrins possess the same terminal substituents as \(\text{NB-ZnP2 and NB-ZnP3}\). However, the phenyl porphyrins, \(\text{NB-ZnP6 and NB-ZnP7}\), should adopt an idealised orthogonal arrangement with respect to the porphyrin plane and in doing so the \(\pi\) systems of the porphyrin and \(meso\) substituents will no longer overlap. The absorbance spectra of the phenyl porphyrins is bathochromically shifted with respect to \(\text{ZnTPP}\). There was a significant change in the fluorescence profile although the lifetimes
were only slightly altered. The most perceptible change was the triplet lifetime of NB-ZnP7 which was double that of ZnTPP. Clearly there is a contribution from the meso substituents even though the conformation prevents coupling of the $\pi$ systems. Electrochemical studies indicated the stabilisation of both the HOMO and LUMO orbitals for both phenyl porphyrins.
2.7 Bibliography


56 Jonathon Rochford, Ph.D. thesis, Dublin City University, Dublin 9, **2004**.
<table>
<thead>
<tr>
<th>No.</th>
<th>Authors</th>
<th>Journal</th>
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Chapter 3

The synthesis, photochemistry and electrochemical properties of a series of thiophene based dyads and the corresponding metal carbonyl complexes.

Chapter three commences with a general introduction to Sonogashira-Hagihara type cross coupling reactions. This is followed by a literature survey on the synthesis and photochemistry of thienyl based organometallic systems. The synthesis of the novel systems produced for this study is then described and the photophysical properties are discussed. Electrochemical data are also presented. The photochemistry of the Co$_2$(CO)$_6$ complexes are examined by steady state photolysis in the presence of a trapping ligand. Three of the complexes were studied by TRIR on a picosecond timescale and the quantum yields for the CO loss process was determined at a range of excitation wavelengths.
3.1 Literature Survey

3.1.1 Cross coupling reactions

Organometallic chemistry has provided several new methods to carry out carbon-carbon (or carbon-heteroatom) bond formation. Such processes, generally termed cross coupling reactions, have found a central place in organic synthesis with their scope increasing year on year. The Sonogashira-Hagihara reaction involves the coupling of terminal alkynes with aryl or vinyl halides under palladium catalysis (Rxn. 1), a procedure which has not changed much since originally reported in 1975.\(^1\)

\[
R - X + \begin{array}{c} \text{alkyne} \\ \hline \end{array} R' \xrightarrow{\text{Pd(0)}} \begin{array}{c} \text{R} \\ \hline \end{array} \begin{array}{c} \text{R'} \\ \hline \end{array} + HX
\]

Rxn. 1 Sonogashira – Hagihara reaction.

Other important cross-coupling reactions include the Negishi,\(^2\) Suzuki-Miyaura,\(^3\) Heck\(^4\) and Stille\(^5\) reactions. A very detailed general overview of palladium catalysed alkynlation reactions has been compiled\(^6\) and a review of palladium catalysed cross coupling reactions in organoboron compounds has also been published.\(^7\) Further still, the use of Negishi cross coupling reactions in the generation of a new binding site in a \(\text{Ru(bpy)}_2\) complex was reported,\(^8\) while a detailed review of regioselective cross coupling reactions of multiple halogenated nitrogen-, oxygen-, and sulphur-containing compounds can also be found in press.\(^9\)

The Sonogashira coupling is a catalytic process performed in the presence of an amine base, using a palladium(0) complex and generally requires copper iodide as a co-catalyst (Scheme 1). Initially the palladium catalyst is oxidised (to Pd(II)) and a cyclic reaction follows. Oxidative addition of the organic halide to the palladium takes place giving a Pd(II) intermediate. In parallel, Cu(I) coordinates to the alkyne terminal end and transmetallation occurs, so called because the nucleophile is transferred from the metal in the organometallic reagent to the palladium and the counterion moves in the opposite direction. Reductive elimination yields the final coupled product, with the Pd(0) catalyst ready for another cycle.
Scheme 1  Sonogashira cross coupling reaction mechanism, using the formation of 2-phenylethynyl)thiophene (NB-L1) as an example.

It is often convenient to use a stable and soluble Pd(II) source such as Pd(PPh3)2Cl2 instead of Pd(0). This precursor is reduced in situ to give the coordinately unsaturated catalytically active Pd(0) species. The reduction of Pd(II) to Pd(0) can be achieved with an amine. A stoichiometric excess of an amine, usually Et3N, serves two purposes: it acts as a base to trap the halide and as a reducing agent for palladium.
3.1.2 Functionalised thiophenes

A series of functionalised thiophenes and bithiophenes were synthesised and their non-linear optical properties were studied by both computational and experimental methods. The thiophenes contained combinations of dimethylamino and dimethylhydrazono \( \pi \)-donors along with nitro and dicyanovinyl \( \pi \)-acceptor groups. The first hyperpolarisability, \( \beta \), is an important aspect for second-order NLO materials as the magnitude of \( \beta \) determines how efficient a given molecule will be in causing quadratic (second-order) NLO effects. The main molecular features for high \( \beta \) is a polarisable framework, such as an aromatic ring substituted with donor (D) and acceptor (A) moieties in a non-centrosymmetric fashion (1-7, Fig. 1). The calculated \( \beta(0) \) values for the lowest energy conformations were found to be in good agreement with experimental \( \beta(0) \) values. Comparison of 1 with 2 revealed that thiophene provides a more efficient delocalisation pathway than benzene. Addition of the imine (-N=CH-) unit to the \( \pi \)-electron conjugating pathway in hydrazone 3 caused a doubling of \( \beta \) with respect to 2. Computational studies also revealed increased conjugation pathlength in 4, with its dicyanovinyl acceptor as opposed to the nitro group in 2, which led to an increase in \( \beta \). Including both the hydrazone and dicyanovinyl in thiophene 5 resulted in a fivefold increase with respect to the 2. Similarly the bithienyl with the hydrazine-dicyanovinyl combination, 6, gave a \( \beta \) value about twice as high as the dimethylamino-nitro derivative, 7. This suggests that thiophenes of this type could be used in NLO materials.
Donor-acceptor conjugated compounds are of considerable interest because they find potential applications in (opto)electronic devices such as field effect transistors and light emitting diodes. Studies have demonstrated that replacing the benzene core with another heterocycle such as thiophene, pyrrole or thiazole resulted in enhanced molecular hyperpolarisabilities. Conjugated thiophene – pyrrole derivatives as donors with appropriate acceptor substitutes have been synthesised as candidates for push–pull systems (8 - 13, Fig. 2). The potential of these conjugated molecules as strong \( \pi \)-electron donor units functionalised with dicyanovinyl were examined. Larger bathochromic shifts of the absorbance maxima in the UV-vis spectra are observed as the acceptor strength of the dicyanovinyl group increases. The position of the dicyanovinyl group on the thiophene ring or on the pyrrole ring can be seen in the absorbance spectra, 8 \( \lambda_{\text{max}} = 454 \text{ nm} \) whereas with 9 \( \lambda_{\text{max}} = 415 \text{ nm} \). The bathochromic shift observed for 8 is due to more extensive electron delocalisation. The position of the absorbance bands is largely affected by the substitution position of the dicyanovinyl group along with the group that was substituted onto the nitrogen atom of the pyrrole ring. Donor-acceptor substituted thienylpyrroles

\[ \text{Figure 1} \quad \text{Functionalised thiophenes and bithiophenes of the form (D-}\pi\text{-A).} \]
have previously been shown to demonstrate strong solvatochromic behaviour and compounds 8 - 13 are no exception. Compounds 8 and 12 were examined in a range of 15 solvents. Respective energy shifts of $\Delta v = +1130$ cm$^{-1}$ and +1263 cm$^{-1}$ were observed for their CT absorbance bands indicating positive solvatochroism. All compounds displayed two oxidative processes ascribed to the formation of the radical cation of the pyrrole but extraction of subsequent electrons gives rise to an irreversible process. As a consequence of the destabilising effect of the electron withdrawing dicyanovinyl group compounds 8 and 10-13 displayed their first oxidation between +0.46 – 0.68 V vs. Fe/Fe$^+$. The reduction of the thienylpyrroles was reversible one-electron process. A clear cathodic shift in the reduction peak was observed as the donor strength in the substituent group on the nitrogen of the pyrrole increases. Hyper-Rayleigh scattering was used to measure the first hyperpolarisability, $\beta$, of the compounds. For compounds 8 and 9 values of $526 \times 10^{-30}$ and $85 \times 10^{-30}$ esu respectively were obtained, which indicates that the positioning the dicyanovinyl group on the 5’ position of the thiophene ring leads to larger nonlinearity than the same group on the 5-position of the pyrrole. The $\beta$ value for 10 - 13 increased with the donor strength of the substituent on the nitrogen atom of the pyrrole ring along the series with 10 ($364 \times 10^{-30}$ esu) < 11 ($439 \times 10^{-30}$ esu) < 12 ($651 \times 10^{-30}$ esu).

![Chemical structures](Image)

**Figure 2** Conjugated thiophene-pyrrole push – pull systems.

8: $R_1 = \text{CH} = \text{C}(\text{CN})_2$, $R_2 = \text{H}$

9: $R_1 = \text{H}$, $R_2 = \text{CH} = \text{C}(\text{CN})_2$

10: $R_3 = \text{H}$

11: $R_3 = 4$-$\text{MeO}$

12: $R_3 = 2,4$-$\text{diMeO}$

13: $R_3 = 4$-$\text{F}$
3.1.3 Thiophene acetylene systems

A series of push-pull substituted oligo(2,5-thienyleneethynylene)s (OTE’s) with alkylthio groups (R₁) and nitro groups (R₂) were synthesised (14 - 18, Fig. 3) and their electronic properties examined. The donor-acceptor substitution caused polarisation within the molecule which was evident from the Δ δ (13C) values of the acetylenic carbon atoms. The Δ δ (13C) values were found to decrease with increasing chain length (n = 2, 3, 4) as extension of the conjugation led to increased distance between D and A, which therefore decreased the partial dipole moment at the chain ends. Further evidence for the D-π-A interaction can be observed in the absorbance spectra where intramolecular charge transfer (ICT) bands were observed. The parent compound 14, displays a λmax value of 317 nm whereas the substituted OTE 15 displays a λmax value at 413 nm. The effect is strong for the small distance between the donor and acceptor sides in compound 15. As the number of repeating units increases the extent of the bathochromic shift decreases (λmax 15 = 413 nm, 16 = 426 nm, 17 = 427 nm, 18 = 428 nm).

![Figure 3 Donor-acceptor substituted conjugated thienyl oligomers (D-π-A type).](image-url)

Rodríguez et al. synthesised a large body of conjugated 2-arylethenyl and 2-arylethynyl thiophene structures (19 - 34, Fig. 4) in order to improve the nonlinear optical properties of these types of molecules. All compounds in the series were synthesised via a sequence of heterocoupling (Sonogashira) or oxidative homocoupling reactions. Compounds 19 and 20 (Fig. 4) were initial conjugated 2-thienyl end-capped structures. The conjugation effect through the double or triple bond to the thiophene ring and the conjugated chains were considered. Extension of the 2-thienyl end-capped structures (to produce 23, 24 and 25) was carried out by coupling 21 and 22. The para connection of the two acetylenic units (in
26 and 27) guaranteed conjugated electronic communication in the follow-on compounds 28 – 34, where 3, 4, 8 and 9 were coupled to 2,5'-thienyl positions. The conjugated molecules which integrate the thiophene rings and the end-capped N,N-dimethyaminophenyl unit (28 and 29) were constructed as this type of compound showed intrinsic electronic properties including luminescence and charge transport characteristics. Compound 19 exhibited a low quantum yield of fluorescence while for 20 no emission fluorescence was observed. The ethenyl conjugate, 23, displayed two emission bands at \( \lambda_{\text{max}} = 427, 454 \) nm whereas the ethynyl conjugate molecule, 24, possessed a unique emission band at \( \lambda_{\text{max}} = 421 \) nm, with higher quantum yield. Compound 25 showed two fluorescence bands at \( \lambda_{\text{max}} = 390, 410 \) nm with a lower quantum yield than that of 24. The reported quantum yields were 0.29, 0.36 and 0.30 for 23, 24 and 25 respectively. All the 2,5 disubstituted thiophene conjugates (28 - 34) showed fluorescence emission bands with some noteworthy points. Each of the compounds 32 - 34 displayed two emission bands while compounds 28 - 31 showed just a single emission band. Increasing the number of ethynylphenyl units as in 28, 29 and 32 - 34 caused a significant increase in the emission quantum yield (0.20, 0.42 and 0.54 for 32 - 34 respectively). In compounds 30 and 31, where the double bond was replaced by a triple bond, an increase in quantum yields was observed (in order: 0.10 and 0.34). The authors have shown that by controlling the structure and dimensions of a compound the fluorescence properties can be fine tuned.
Figure 4  Conjugated 2-arylethenyl and 2-arylethynyl thiophene structures.
Several structures of π-conjugated polymers were examined to measure the impact that regioregularity had on the photoluminescence. Compounds 35 and 36 (Fig. 5) were synthesised from monomers through selective formation of carbon – carbon bonds at specific locations. Three chain sequences of the polymers were made: 1: the head-to-tail sequence 35, 2: the head-to-head and tail-to-tail sequence 36, and 3: a regiorandom sample which contained head-to-head and head-to-tail sequences in a ratio of about 50:50. The absorbance spectra of 35 and 36, which were almost identical, suggested essentially the same conjugation length along the π-conjugated backbone in both polymers. The rigidity of the molecules as a result of the extended π-π conjugation was calculated. Using the Mark-Houwink equation values of 1.06 and 0.91 were obtained for 35 and 36 respectively. This indicated that the head-to-tail chain sequence of 35 had a slightly more rigid conformation in dilute solution. The radius of gyration, $R_g$, used to measure the stiffness of a polymer ($R_g/M_w$) also confirmed that 35 was more rigid. The chain stiffness of the regiorandom sample fell between that of 35 and 36 for both the Mark-Houwink and $R_g/M_w$ values. Both 35 and 36 showed nearly identical absorbance spectra with the $\lambda_{\text{max}}$ observed at 414 and 415 nm. They also displayed almost identical photoluminescence (PL) profiles with the emission $\lambda_{\text{max}}$ at 453 and 478 respectively. However the quantum efficiency of 35 was higher than that of 36 ($35 \Phi_n = 0.59, 36 \Phi_n = 0.53$), which the authors attributed to the relative molecular stiffness of the molecule. Both regioregular compounds had higher quantum efficiencies than that of the regiorandom compound ($\Phi_n = 0.42$). This indicated that the PL efficiency was affected not only by the relative content of head-to-tail sequences that determine the chain rigidity, but also by the detailed linkages between the chain sequences. The absorbance and fluorescence spectra of a solid state film of 36 are both red shifted in comparison to the film of 35. It appeared that the more symmetrical chain sequence (head-to-head and tail-to-tail) of 36 allowed for better packing in the solid state. In the solid state the fluorescence of 36 was ~2.5 times stronger than that of film 35 and both have significantly stronger emission than the regiorandom sample. Thus, photoluminescence enhancement is dependent on structural regioregularity, especially in the solid state.
The homologous series 37 - 40 (Fig. 6) are well defined oligomers, where tetramer 40 is the longest of the series and lacks the terminal silyl-protected triple bond, were synthesised by palladium-catalysed cross-coupling reactions (Sonogashira). Their optical and electrochemical properties were compared to that of a structurally related series of oligo(3-hexylthiophene)s as it gives insight into common and deviating physical properties between the two series. Increasing chain length of the conjugation system resulted in a progressive bathochromic shift of the absorbance maxima with enhancement of the extinction coefficient in steps of about 20,000 M$^{-1}$ cm$^{-1}$. This is almost equal to the extinction coefficient of ethynylated bithiophene ($\varepsilon = 18,800$ M$^{-1}$ cm$^{-1}$). While 37 displayed an absorbance $\lambda_{\text{max}}$ at 333 nm ($\varepsilon = 18,800$ M$^{-1}$ cm$^{-1}$), the other homologues increased in order 38 ($\lambda_{\text{max}} = 392$ nm, $\varepsilon = 40,800$ M$^{-1}$ cm$^{-1}$), 39 ($\lambda_{\text{max}} = 471$ nm, $\varepsilon = 54,400$ M$^{-1}$ cm$^{-1}$) and 40 ($\lambda_{\text{max}} = 427$ nm, $\varepsilon = 78,700$ M$^{-1}$ cm$^{-1}$). The emission maxima were red-shifted with increasing chain length. The bithiophene, 37, displayed a $\lambda_{\text{em}}$ at 410 nm and this was shifted steadily to longer wavelength for the higher homologues. The $\lambda_{\text{em}}$ for the dimeric compound, 38, shifted by 59 nm to 469 nm, with trimeric 39 bathochromically shifted to $\lambda_{\text{em}} = 510$ nm ($\Delta\lambda_{\text{em}} = 41$ nm with respect to 38). For the tetrameric compound, 40, the change in emission maxima becomes less pronounced with the difference between the highest analogues, 39 and 40, only 11 nm ($\lambda_{\text{em}}$ of 40 = 521 nm). No overall trend was observed for the fluorescence quantum yields (37, 38, 39, 40: $\Phi = 0.08$, 0.46, 0.36, 0.43 respectively). The stepwise increase of the conjugation chain length led to an increased number of redox potentials which lay closer together. Monomer 37 displayed only one
oxidation wave ($E^\circ = 0.75 \text{ V vs. } \text{Fc/Fc}^+$), 38 and 39 had two and three waves respectively (38: $E^\circ = 0.56, 0.77 \text{ V vs. } \text{Fc/Fc}^+$, 39: $E^\circ = 0.50, 0.62, 1.00 \text{ V vs. } \text{Fc/Fc}^+$) and the tetramer 40 had four oxidation waves ($E^\circ = 0.45, 0.50, 0.77, 0.94 \text{ V vs. } \text{Fc/Fc}^+$). No reduction waves were observed down to potentials of -2.1 V vs. Fc/Fc$. A correlation of the maximum absorbance and emission energies versus the inverse number of atoms in the conjugation backbone presents clear linear relationships. There is a systematic change in the spectral features but particularly in the emission and oxidation behaviours. The influence of the triple bonds becomes more pronounced with increasing chain length.

![Diagram of molecular structures](image)

**Figure 6**  Oligomeric series (monomer to tetramer) of ethynyl bithiophenes.

Inspired by structures of metalloproteins, Toyota and co-workers used Sonogashira and Suzuki coupling techniques to synthesise a spacer, 1,4-bis(2-ethynyl-3-thienyl)benzene (ETB) (41, Fig. 7), which has a phenylene axis and a pair of thien-3-yl units at both ends of the axis.$^{16}$ Selective introduction of substituents at the terminal sp-carbon and/or 5-position of the thiophene rings (42- - 55, Fig. 7) made an easily tuneable spacer. UV-vis spectra of compounds were compared to the parent 41 (where R = H). Compounds 42, 49
and 53, the trimethylsilyl series, showed a bathochromic shift in the order 49 > 42 > 53. Compared to 49 a significant red shift was observed in compound 42 with a concomitant increase in extinction coefficient which indicated the existence of increased π-conjugation through the central phenylene unit. Compound 53 with the biphenyl moiety showed the largest bathochromic shift among the three trimethylsilyl substituted derivatives however the difference in $\lambda_{\text{max}}$ between 53 and 41 is relatively small suggesting that the extension of the π-system is hindered by the lack of co-planarity in the biphenyl species. The phenylethynyl derivatives 46, 47, 51, 52 and 55 again showed a similar absorbance profile with the $\lambda_{\text{max}}$ shifting to lower energy in the order 47 > 46 > 51 > 52. Similar to the previous series, the spectrum of 46 exhibited the larger molar absorbances and 55 showed very little change compared to 46. The pyridyl derivatives, 43-45, 50 and 54, gave comparable results. Compound 43 displayed the largest extinction coefficient, with the others following the order 43 > 45 > 44. As expected, 54 did not show a significant red-shift compared to those of compounds 41 or 51 whereas the spectra of 43-45 did show large bathochromic shifts. This indicates that significant π-conjugation through the central phenylene moiety is possible.

![Chemical structures](image)

Figure 7  ETB (1,4-bis(2-ethynyl-3-thienyl)benzene) spacers with various groups attached at both ends of the axis.
A new class of radial oligothiophenes (57 - 60, Fig. 8) with oligophene “arms” (56, Fig. 8) around a central aromatic core attached with alkynyl linkages were reported. These radial “starlike” molecules included ethynyl units bound directly to the core and were expected to support extended \( \pi \)-conjugation of the molecule as well as adding coplanarity to the molecule. Both the absorbance and emission spectra were examined. Increasing the number of oligothiophene arms around the arene (benzene or thiophene) core caused the \( \lambda_{\text{max}} \) of the lowest \( \pi-\pi^* \) transition to be red shifted (57: \( \lambda_{\text{max}} = 400 \text{ nm} \), 59: \( \lambda_{\text{max}} = 458 \text{ nm} \)). The \( \lambda_{\text{max}} \) of the unappended thiophene arm, 56, was observed at 374 nm suggesting that the overall coordination of the oligothiophene arms to the arene core induced delocalisation of the \( \pi \) system. Solid state spectra of the homologues were also bathochromically shifted with respect to solution phase which is attributed to enhanced planarity of the molecule in the solid state. A similar trend was observed for the emission spectra, each displaying a red shifted emission \( \lambda_{\text{max}} \) as the number of thiophene rings increased (\( \lambda_{\text{max}} \) 57 = 520 nm, \( \lambda_{\text{max}} \) 59 = 615 nm) which were further bathochromically shifted in the solid state.

![Figure 8](image-url) 

*Figure 8* Radial oligothiophenes with arene core.
### 3.1.4 Bonding in metal carbonyl compounds

In order to discuss the bonding in metal carbonyl complexes, the carbon oxygen bond must first be examined. In carbon monoxide there is a $\sigma$-bond between the carbon and oxygen atoms and a lone pairs of electrons on each of the two atoms. There is also a doubly degenerate $\pi$-bonding orbital. The result of which is a triple bond ($\sigma^2(\pi_x)^2(\pi_y)^2$ (Fig. 9 (a))). However this is a polar bond, and in the $\pi$-orbitals the electrons are almost four times as likely to be near the oxygen as near the carbon. The low dipole moment observed for carbon monoxide can be explained by the bonds polarity compensating for the strongly directional lone pair on the carbon atom. CO is an example of a good $\pi$ acceptor. Such ligands are of great significance in organometallic chemistry as they form strong metal-ligand bonds.

In forming a metal-carbon $\sigma$-bond the metal employs its $nd$, $(n+1)p$ and $(n+1)s$ vacant metal orbitals. The metal must possess vacant d-orbitals that can overlap with the lone pair on the carbon and this may be regarded as the formation of a metal-carbon $\sigma$-bond of the donor acceptor type. In the metal carbonyl there are filled non-bonding d-orbitals on the metal which have the correct symmetry to overlap with the empty orbitals of the CO, this orbital is the CO $\pi^*$, a low-lying $\pi$-antibonding orbital of the carbon monoxide and it accepts electron pairs from the occupied metal d-orbitals (Fig. 9 (b)). As a result of this additional $\pi$-bond the $d_\pi$ electrons that were metal centred now sometimes reside on the ligand. The metal has now donated electron density back to the ligands. This is referred to as back bonding and is a feature of M – L bonds where L is an unsaturated molecule. Back bonding allows electron density on the metal shift back to the ligands. As well as an additional $\pi$-bond, the transference of charge from the metal can be seen as a means of strengthening the original $\sigma$-bond (it contributes principally to the total bond energy) by removal of unfavourable charge separation induced by the donor $\sigma$-bond. This produces a “synergic” interaction between the two types of bonds and it is this interaction that accounts for the most part of the metal-carbon bond strength.
In addition to the previously discussed linear M–C–O bond, many metal carbonyl compounds possess a carbon monoxide group bonded to two or more metal atoms. This bridging effect in carbonyl compounds is generally confined to derivatives of the first row transition metals. Simplistically it can be assumed that bridging carbonyl groups contribute only one electron to each of the metal atoms forming $\sigma$-bonds with the metal electrons. The nature of the $\pi$-bonding is a little more complicated. The carbon-oxygen bond order is reduced as evidenced by a shift in CO stretching frequencies to $\sim 1850 \text{ cm}^{-1}$. Another important type of bond found in metal carbonyls is the metal-metal bond. It is sometimes the only bond between two halves of a metal carbonyl but often found in conjunction with bridging carbonyl groups. With the exception of vanadium hexacarbonyl, all binary carbonyls obey the inert gas rule with (a) terminal carbonyl groups each contributing a pair of electrons to the outer of the metal atoms, (b) bridging carbonyls each contributing one electron to each of the metal atoms and (c) covalent metal-metal bonds formed by one electron from each metal atom bringing the total number of electrons to that of the next inert-gas shell.
3.1.5 Dicobalt hexacarbonyl complexes

The pioneering work of Reppe\textsuperscript{18} and Hübel\textsuperscript{19} in the field of alkyne – metal chemistry in the 1940’s and 1960’s respectively revealed the structural diversity of alkyne oligomerisation at metal centres. Complexes of the ($\mu_2$-alkyne)Co$_2$(CO)$_6$ series are among the earliest known organometallic compounds.\textsuperscript{20} The dicobaltatetrahedrane, ($\text{RC} \equiv \text{CR'}$)Co$_2$(CO)$_6$, is the main product of alkynes reacting with Co$_2$(CO)$_8$ at room temperature. One of the most widely reported and studied of these dicobalt hexacarbonyl complexes being diphenylacetylene dicobalt hexacarbonyl, ($\mu_2$-PhC\equivCPh)Co$_2$(CO)$_6$.

Dicobalt octacarbonyl is the simplest closed shell cobalt carbonyl, containing two types of carbonyl groups, i.e. bridge and terminal carbonyl groups as shown in figure 10 (a). Alkynes possess a pair of perpendicular mutually degenerate p-\(\pi\) orbitals. The reaction of an alkyne with dicobalt octacarbonyl replaces two bridge carbonyl groups to form the organometallic complex (Rxn. 2, Fig. 10 (b)). Bridge bonding observed in ($\mu_2$-alkyne)Co$_2$(CO)$_6$ complexes are thought to arise from a combination of forward donation from the two bonding $\pi$ molecular orbitals of the alkyne into the unfilled metal d orbitals and back donation from the filled metal orbitals into the vacant antibonding $\pi$ molecular orbitals of the alkyne.\textsuperscript{21}

\textit{Rxn. 2} \quad \text{RC} \equiv \text{CR'} + \text{Co}_2(\text{CO})_8 \rightarrow (\mu_2-\text{RC} \equiv \text{CR'})\text{Co}_2(\text{CO})_6 + 2\text{CO}↑

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure10.png}
\caption{(a) Structure of dicobalt octacarbonyl with bridging and terminal carbonyl groups, (b) structure of alkyne dicobalt hexacarbonyl, ($\mu_2$-R$_2$C$_2$)Co$_2$(CO)$_6$ showing the axial (ax) and equatorial (eq) carbonyl groups.}
\end{figure}
Sly reported the molecular configuration of diphenylacetylene dicobalt hexacarbonyl, one of the first molecules to exhibit a multi-point attachment of a single organic molecule to more than one metal. The molecule was found to have six-fold coordination about each cobalt atom in a distorted octahedral with the C-C bond of the acetylene approximately normal to the Co-Co bond axis. The coordination about the acetylene carbon atoms is four-fold in a distorted tetrahedral configuration. This gives approximate $C_2v$ symmetry to the molecule, except for the benzene rings. With most symmetric alkynes the molecules possess $C_2v$ symmetry with distorted octahedral symmetry about the individual cobalt atoms.

A more recent theoretical study of the alkyne-bridged complex, $(\mu_2-C_2H_2)Co_2(CO)_6$, identified significant population of a Co-Co antibonding orbital along with Co-$\pi^*$ back bonding. The authors used complete active space (CAS) methods along with Hartree-Fock and hybrid density functional theory (DFT) calculations for this study, as standard DFT and quantum theory of atoms in molecules (QTAIM) methods, although useful, were insufficient to reveal the fine detail in the region between bridged metal atoms. The occupation of bonding and antibonding orbitals in the CAS molecular calculations suggested a rather more complex picture of metal-metal and metal-ligand bonding than might be initially inferred. Using CAS in conjunction with QTAIM, a deeper insight into the bonding was gained. Surprisingly, there was no bond critical point (bcp) observed in the region between cobalt nuclei, although four Co-C$_{\text{alkyne}}$ bonds were observed in the analysis, along with all other expected bond critical points (Co-C$_{\text{CO}}$, C-C, C-O and C-H). This indicated the presence of two three-membered metallocycles in the Co$_2$C core, sometimes referred to as a “butterfly arrangement”. Hartree-Fock calculations explore metal-metal bonding where a value of 1.0 indicates a single bond. The authors, who calculated a value of 0.26 for $\delta$(Co,Co), using an adjusted theoretical method, state that the atomic overlap data suggested a weak but non-zero overlap between the cobalt atoms. Another diagnostic tool which calculates the ratio of potential to kinetic energy density at bond critical points was employed. A value of less than one indicates closed shell interaction while a value of greater than two indicates a shared or covalent interaction. A value of 1.34 at the mid-point of the Co-Co vector and other values across the vector were observed. Consistent with other results, it points to some covalent character in the metal-metal region. The authors suggested that the complex was best described as a singlet.
diradical with partial occupation of both bonding and antibonding orbitals between cobalt atoms.

The structure of ($\mu_2$-alkyne)Co$_2$(CO)$_6$ derivatives are based on a central Co$_2$C$_2$ tetrahedrane with an external “R” group on each carbon and three terminal carbonyl groups on each cobalt (Fig. 10 (b)). The Co$_2$C$_2$ tetrahedrane in an ($\mu_2$-R$_2$C$_2$)Co$_2$(CO)$_6$ complex had 12 skeletal electrons localised along its six bonds that include four Co-C bonds, one C-C bond and one Co-Co bond. As discussed above the Co-Co bond is considered to be a formal single bond however some singlet diradical character of the Co-Co interaction has been observed. Using DFT calculations, model complexes of the form ($\mu_2$-R$_2$C$_2$)Co$_2$(CO)$_n$ ($n < 6$) were used for a theoretical study investigating the preferred structure for alkynyl dicobalt hexacarbonyl complexes. Structures of ($\mu_2$-C$_2$H$_2$)Co$_2$(CO)$_6$ (61), ($\mu_2$-C$_2$H$_2$)Co$_2$(CO)$_5$, ($\mu_2$-C$_2$H$_2$)Co$_2$(CO)$_4$ were investigated (formal Co=Co double and Co≡Co triple bonds were required to give both cobalt atoms the favoured 18-electron configurations in the pentacarbonyl and tetracarbonyl respectively). An eclipsed C$_2v$ structure was the preferred structure for ($\mu_2$-C$_2$H$_2$)Co$_2$(CO)$_6$ (61, Fig. 11) with two axial carbonyls approximately trans to the Co-Co bond and the remaining four carbonyls are equatorial in approximate trans positions relative to the Co-C bonds attached to the acetylene carbon. The Co-CO bond lengths were predicted to be longer for those in equatorial positions (Co-CO$_{eq} \sim 0.04$ Å longer than Co-CO$_{ax}$) suggesting that the acetylene ligand has a stronger trans effect than the Co-Co bond. Three structures were found for the pentacarbonyl derivative, ($\mu_2$-C$_2$H$_2$)Co$_2$(CO)$_5$. The lowest energy structure is derived by removal of an equatorial carbonyl group (a carbonyl group trans to the acetylene) and can be referred to as eq-($\mu_2$-C$_2$H$_2$)Co$_2$(CO)$_5$. The second is a C$_2v$ singly bridged ($\mu_2$-C$_2$H$_2$)Co$_2$(CO)$_4$(μ-CO) structure. The bridging carbonyl group exhibits a relatively low ν(CO) stretch at 1878 cm$^{-1}$ typical for bridging carbonyl groups compared to terminal carbonyl groups. The third pentacarbonyl structure is the result of loss of an axial carbonyl group, ax-($\mu_2$-C$_2$H$_2$)Co$_2$(CO)$_5$ and lies a predicted ~ 10 kcal above the equatorial structure. In both the axial and equatorial pentacarbonyl species one cobalt atom is assigned the favoured 18-electron configuration while the other cobalt atom bearing only two terminal carbonyls has only a 16-electron configuration. Removal of two carbonyl groups from the parent hexacarbonyl species resulted in ($\mu_2$-C$_2$H$_2$)Co$_2$(CO)$_4$ to give six different structures.
The three lowest energy structures are derived by removal of two carbonyl groups from different cobalt atoms so that each have two Co(CO)_2 units in their structure.

Figure 11  \((\mu_2\text{-}C_2H_2)\text{Co}_2(\text{CO})_6\) (61) with proposed C_2v symmetry.

A series of oligothiophene derivatives were synthesised in which two dicobalt hexacarbonyl acetylides were π-conjugated onto both terminals of the oligothiophene. A variety of substituents were grafted onto the oligothiophenes to tune their physical properties. Heck coupling techniques were used to produce the organic compounds (62a – 66a, Scheme 2) and reaction with dicobalt octacarbonyl gave the alkyne dicobalt hexacarbonyl derivatives (62b – 66b, Scheme 2). The absorbance spectra of the oligothiophene moieties displayed moderately intense high energy transitions and a very intense lower energy transition which the authors attributed to π − π* localised excitation of the heteronucleus and π − π* transitions of the conjugated π – system, respectively. The \(\lambda_{\text{max}}\) values of the higher energy bands were blue-shifted on increasing the number of thienyl units (\(\lambda_{\text{max}}\) 62a = 305 nm, 64a = 257 nm, 66a = 254 nm) with similar trends observed for the phenyl substituted oligomers. The complexes (62b – 66b) exhibited three characteristic bands: a moderately intense high-energy band, a strong medium-energy band and a weak low-energy band. The high energy bands were ascribed to the π − π* localised excitation within the organic component while the medium and low energy bands were
attributed to metal to ligand (d_{Co}π^*_{ligand}) charge transfer transitions. Electrochemical studies of 62a – 66a exhibited one highly irreversible oxidation process (two for 65a), the potential of which decreases gradually on going from 62a to 64a to 65a in the hexynyl substituted oligothiophene series and from 63a to 65a in the phenylethynyl substituted series, indicating the decrease of the π-conjugation length in serial order. The complexes (62b – 66b) exhibited two oligothiophene based oxidation processes (one for 63b) between -0.2 and +1.5 V vs. Ag/AgCl, and one reduction process of the metal moiety between 0.0 and -1.6 V vs. Ag/AgCl, which was not observed for the oligothiophenes. The complexes only possess one irreversible reduction process compared to the two reductions commonly observed in these bimetallic systems the authors suggested that the redox centres were independent of each other. The lack of electronic communication between the metal centres is attributed to the reduction process followed by fast chemical reactions via an EC mechanism.

Scheme 3  Synthesis of thienylethynyl ligands and corresponding bimetallic complexes.
Ferrocene is an electron donating group where the ferrocenyl donor group can be linked via an electron-rich backbone to a polyaromatic acceptor moiety. The attachment of adjacent organometallic moieties via alkyne linkages results in electronic interactions between metal atoms. These complexes are of interest because of the possibility of charge transfer along a conjugated backbone and the potential for tuneable redox behaviour. The modification of ferrocene substituted (µ₂-alkyne)Co₂(CO)₆ complexes enabled the assessment of the effect of structural changes imposed by changing the position and substituents on ferrocenyalkynes. The ferrocenyalkynyl ligands were synthesised by standard coupling methods followed by treatment with cobalt octacarbonyl to produce the complexes 67 - 72 in figure 12. The incorporation of one or two dicobalt carbonyl moieties into the alkynyl chain caused a reduction in triple bond character observed as a downfield shift in the proton and carbon NMR spectra of the products. Crystal structures of 68, 69 and 72 were obtained and observed Co-Co bond lengths were in the range 2.46 – 2.47 Å, in agreement with previously reported dicobalt systems bridged by perpendicular alkynes. The interaction of the alkyne with Co₂(CO)₆ units resulted in delocalisation of the electron density onto the Co₂ unit which caused a lengthening of the alkyne bond, consistent with loss of triple bond character as observed in the NMR. In complex 68 the free alkyne unit retains its linearity as expected and the relevant bond length was consistent with the retention of its triple bond character (1.20 Å). Phosphine substitution of carbonyl ligands in the dicobalt hexacarbonyl complexes occurred. Complex 67 was treated with 1 equivalent of 1,1-bis(diphenylphosphino)methane (dppm) and 1.5 equivalents of 1,1-bis(diphenylphosphino)ferrocene (dppf) to produce the phosphine substituted ethynylferrocene : dppm in 1:1 ratio and ethynylferrocene : dppf in 2:3 ratio respectively. In this manner the electronic environment of the metal atoms can be modified via replacement of some carbonyl groups by suitable chiral phosphine ligands.
Coleman et al. synthesised a series of pyrene-thiophene dyads and their corresponding dicobalt hexacarbonyl complexes (73ab – 76ab, Fig. 13). In the UV-vis absorbance spectra a high energy transition was observed between 320 – 400 nm and ascribed to the $\pi - \pi^*$ transitions within the pyrenylacetylene chromophore. Coordination of dicobalt carbonyl resulted in broader, less well-defined spectra with additional weak d-d bands in the range 580-600 nm that extended to approximately 700 nm. Visible excitation led to luminescence for all compounds in the series. No shift was observed in the emission bands following complexation which suggested the origin of the emission band is ligand based. At room temperature all compounds were found to be strongly luminescent. Compounds 73a and 74a displayed two emission bands at 404, 425 nm and 410, 430 nm respectively. For 75a and 76a a single intense emission band, at 503 and 612 nm respectively, was observed with significantly larger Stokes shifts (~3800 and ~4600 cm$^{-1}$ respectively) indicating that the aldehyde and dicyanovinyl terminal units had a destabilising effect. The bathochromic shift in emission maxima, on altering the terminal moiety, was attributed to the electron accepting ability of the dicyanovinyl unit. Emission lifetimes were measured as 0.16, 0.64, 0.88 and 1.16 ns of 73a, 74a, 75a and 76a. Following coordination with Co$_2$(CO)$_6$ a large reduction in the emission intensity (> 95 %) was observed. Emission quenching had been previously reported for metal carbonyl complexed fluorescent organic compounds. Low temperature (77 K) emission studies showed no change in the emission bands of 73b and 74b. However the emission band of 75b was blue shifted by 2650 cm$^{-1}$ to
444 nm while the emission band of 76b was blue shifted by \(\sim 2890 \text{ cm}^{-1}\) to 520 nm. The authors attributed quenching to energy transfer to the cobalt carbonyl system. All compounds (73a\(\text{b} \rightleftharpoons 76a\(\text{b}\)) exhibited an oxidation in the range +1.0 – 1.1 V vs. Ag/Ag\(^+\), which was assigned to the irreversible oxidation of the pyrene unit. Oxidation at high positive potentials led to the deposition of a film onto the working and counter electrode surfaces. This suggested that electropolymerisation occurred at high positive potentials, a process observed in other thiophene systems. An irreversible oxidation process is observed in the range +0.55 – 0.70 V vs. Ag/Ag\(^+\) in all cases following complexation (73b – 76b). This was assigned to the oxidation of the cobalt metal centre. Steady state photolysis was carried out on 73b – 76b with IR monitoring. Irradiation at \(\lambda_{\text{exc.}} > 520 \text{ nm}\) in the presence of \(\text{PPh}_3\), resulted in bleaching of the parent absorbance bands together with generation of product bands assigned to the pentacarbonyl species. Subsequent irradiation at \(\lambda_{\text{exc.}} > 400 \text{ nm}\) caused further bleaching of the parent bands and an increase in intensity of the photoproduct. Also observed under these conditions were new bands assigned to the tetracarbonyl species.

\[
\begin{align*}
73 & : R = \text{H} \\
74 & : R = \text{Br} \\
75 & : R = \text{CHO} \\
76 & : R = \text{CH(CN)}_2
\end{align*}
\]

![Figure 13](image)

**Figure 13** Pyrenylethynylthienyl compounds and complexes with various end groups.

(\(\mu_2\)-Alkyn)\(\text{Co}_2(\text{CO})_6\) derivatives have been shown to undergo replacement of one or both axial CO groups upon heating with monodentate tertiary phosphines, phosphites and arsines.\(^{28}\) Bidentate ligands, such as fluorocarbon- and hydrocarbon-bridged compounds, reacted similarly but they displaced two or four CO groups. The bidentate ligands tended to occupy equatorial coordination points about the metal atoms either by bridging two
cobalt atoms of the same molecule (Fig. 14, b) or by chelating to one of them (Fig. 14, c).

An investigation into carbonyl substitution reactions of \((\mu_2\text{-RC}≡\text{CR'})\text{Co}_2(\text{CO})_6\) (where R/R’ = H, phenyl or CH$_2$OH) was undertaken for a range of monodentate ligands (L). In each case, heating the \((\mu_2\text{-alkyne})\text{Co}_2(\text{CO})_6\) complexes with the monodentate ligand resulted in the formation the pentacarbonyl product of the form \((\mu_2\text{-RC}≡\text{CR'})\text{Co}_2(\text{CO})_3\text{L}_n\) (Rxn. 3). It was found that further reaction of the alkyln dicobalt pentacarbonyl product with a monodentate ligand resulted in a greater substitution pattern for the complex i.e. disubstituted, trisubstituted and tetrasubstituted complexes of the form \((\mu_2\text{-RC}≡\text{CR'})\text{Co}_2(\text{CO})_4\text{L}_{n-1}\), \((\mu_2\text{-RC}≡\text{CR'})\text{Co}_2(\text{CO})_3\text{L}_2\) and \((\mu_2\text{-RC}≡\text{CR'})\text{Co}_2(\text{CO})_2\text{L}_3\) respectively. Reaction of the ligand substituted carbonyl products \((\mu_2\text{-RC}≡\text{CR'})\text{Co}_2(\text{CO})_6\text{L}_n\) with CO replaced the monodentate ligand to regenerate the parent compound (Rxn. 4).

Fluorocarbon bridged ditertiary phosphines and arsines (denoted as L-L) reacted with \((\mu_2\text{-alkyne})\text{Co}_2(\text{CO})_6\) and produced complexes of form \((\mu_2\text{-alkyne})\text{Co}_2(\text{CO})_4\text{L}_2\) which were ligand bridged. The bidentate ligands f$_4$fos and f$_4$fars (abbreviations pg. xv) produced the bridged disubstituted complexes (Rxn. 5) while further reaction of the disubstituted complex with f$_4$fars/f$_4$fos produced the tetrasubstituted complexes. The reaction of the tetrasubstituted alkynyl dicobalt carbonyl with CO resulted in the regeneration of the disubstituted complex (60 %) by displacement of one bidentate ligand with two CO molecules (Rxn. 6). Complexes of the formula \((\mu_2\text{-alkyne})\text{Co}_2(\text{CO})_4\text{L}(\text{L-L})\) fall into two classes. The first class of \((\mu_2\text{-RC}≡\text{CR'})\text{Co}_2(\text{CO})_4\text{L}(\text{L-L})\) complexes (where L-L = f$_4$fos, f$_4$fars, f$_6$fars, f$_4$AsP and dppm, (abbreviations pg. xv) all had terminal carbonyl stretching bands in their IR spectrum (in the region 1959 – 2038 cm$^{-1}$) similar to those of \((f_4\text{fatos})\text{Co}_2(\text{CO})_6\), and hence the authors assigned a bridged structure to these complexes (Fig. 14, b). The second class of \((\mu_2\text{-RC}≡\text{CR'})\text{Co}_2(\text{CO})_4\text{L}(\text{L-L})\) complexes (where L-L = f$_6$fos and f$_8$fos) had carbonyl stretching bands at higher frequencies (1963 – 2056 cm$^{-1}$), indicating that complexes of this type produced chelates (Fig. 14, b).

\[
(\mu_2\text{-RC}≡\text{CR'})\text{Co}_2(\text{CO})_6 + \text{P(CH}_3\text{O)}_3 \rightarrow (\mu_2\text{-RC}≡\text{CR'})\text{Co}_2(\text{CO})_3(\text{P(CH}_3\text{O)}_3) + \text{CO}
\]

Rxn 3 Substitution with monodentate ligand \(\text{P(CH}_3\text{O)}_3\) producing pentacarbonyl complex.

\[
(\mu_2\text{-RC}≡\text{CR'})\text{Co}_2(\text{CO})_2(\text{P(CH}_3\text{O)}_3)_4 + \text{CO} \rightarrow (\mu_2\text{-RC}≡\text{CR'})\text{Co}_2(\text{CO})_3(\text{P(CH}_3\text{O)}_3)_3
\]

Rxn. 4 Replacement monodentate ligands following reaction with CO.
\[(\mu_2-\text{RC}≡\text{CR'})\text{Co}_2(\text{CO})_6 + f_4\text{fos} \rightarrow (\mu_2-\text{RC}≡\text{CR'})\text{Co}_2(\text{CO})_4(\text{f}_4\text{fos}) + 2\text{CO}\]

\text{Rxn. 5} \text{ Substitution with bidentate ligand producing tetracarbonyl complex}

\[(\mu_2-\text{RC}≡\text{CR'})\text{Co}_2(\text{CO})_2(\text{f}_4\text{fos})_2 + 2\text{CO} \rightarrow (\mu_2-\text{RC}≡\text{CR'})\text{Co}_2(\text{CO})_4(\text{f}_4\text{fos})\]

\text{Rxn. 6} \text{ Replacement bidentate ligand following reaction with 2 equivalents of CO.}

![Figure 14](image)

\text{Figure 14} \text{ Representative structures of (}\mu_2-\text{RC}≡\text{CR'})\text{Co}_2(\text{CO})_6 \text{ complex and the two classes of carbonyl bonded complexes.}

Ford et al. used time resolved spectroscopy (TRIR) to extensively examine the reactive photoproducts produced on irradiation (continuous and flash photolysis) of the hyrdoformylation catalyst precursor \(\text{Co}_2(\text{CO})_6(\text{PMePh}_2)_2\).\textsuperscript{29} The UV-vis absorbance spectrum of \(\text{Co}_2(\text{CO})_6(\text{PMePh}_2)_2\) possessed a characteristic \(\sigma-\sigma^*\) transition with a \(\lambda_{\text{max}}\) at 386 nm, assigned to a metal-metal bonded dimer by analogy to the spectra of similar compounds such as \(\text{Co}_2(\text{CO})_8\). The infrared spectrum shows a carbonyl stretching band centred at 1953 cm\(^{-1}\) with shoulders at \(\sim1928\) and \(\sim1975\) cm\(^{-1}\).

Continuous photolysis (\(\lambda_{\text{exc}} = 365\) nm) of \(\text{Co}_2(\text{CO})_6(\text{PMePh}_2)_2\) in benzene was carried out under different conditions: (1) under an atmosphere of argon, (2) under an atmosphere of CO and (3) under argon with added PMePh\(_2\). (1) Photolysis under argon resulted in small decreases in the 386 nm absorbance band with no new bands appearing in the UV-vis spectrum. In the IR spectrum, similar irradiation caused slow bleaching of the parent band with new broad \(\nu(\text{CO})\) stretches between 1980 and 2040 cm\(^{-1}\), which were tentatively
assigned to the formation of a cobalt cluster complex. (2) Under an atmosphere of CO, photolysis at 365 nm resulted in significant changes on a much faster timescale. The $\text{Co}_2(\text{CO})_6(\text{PMePh}_2)_2$ absorbance at 386 nm decreased in intensity and shifted hypsochromically with concomitant generation of a new absorbance at 340 nm and an isobestic point at 362 nm. This rapidly occurring spectral change ceased after ~90 s irradiation indicating that the system had reached a photostationary state (Rxn. 7). The changes observed were attributed to formation of a dinuclear complex such as $\text{Co}_2(\text{CO})_7(\text{PMePh}_2)$ as the characteristic $\sigma$-$\sigma^*$ transition of a Co-Co bond remained. The IR difference spectrum produced positive peaks at 1987, 2022 and 2078 cm$^{-1}$, which suggested the formation of the PMePh$_2$ loss product as the bands matched well with literature results for the spectrum of $\text{Co}_2(\text{CO})_7(\text{PPh}_3)$. (3) Photolysis of $\text{Co}_2(\text{CO})_6(\text{PMePh}_2)_2$ in benzene under argon with added PMePh$_3$ led to very different spectral changes in the infrared. A decrease in parent bands was observed while new bands formed at 1749, 1770 and 1998 cm$^{-1}$, consistent with the formation of $\text{Co}_2(\text{CO})_5(\text{PMePh}_2)_3$.

$$
\text{Co}_2(\text{CO})_6(\text{PMePh}_2)_2 + \text{CO} \xrightleftharpoons[\text{hv}]{\text{hv}} \text{Co}_2(\text{CO})_7(\text{PMePh}_2) + \text{PMePh}_2
$$

Rxn. 7

Interestingly, continued photolysis ($\lambda_{exc} = 365$ nm) of $\text{Co}_2(\text{CO})_6(\text{PMePh}_2)_2$ in the chlorinated solvent 1,2-dichloroethane (DCE) produced markedly different results. Under an argon atmosphere the intensity of the $\sigma$-$\sigma^*$ transition at 386 nm rapidly decreased with no new bands generated. This is ascribed to photo-induced homolysis of the metal-metal bond to give the mononuclear “17-electron” metal based radicals, $\cdot\text{Co(}\text{CO})_3(\text{PMePh}_2)$ (A, Scheme 3). These radicals can undergo two processes either bimolecular reaction with another such radical to reform the metal-metal bond (B, Scheme 3) or extraction of a chlorine atom from the solvent to form mononuclear chlorinated products (C, Scheme 3). Monitoring the reaction by IR spectroscopy provided further evidence for the formation of chlorinated mononuclear photoproducts. Bleaching of the $\nu$(CO) bands characteristic of $\text{Co}_2(\text{CO})_6L_2$ with concomitant growth of bands at 1981 and 1917 cm$^{-1}$ were observed
which indicated the formation of Co(CO)\(_3\)(PMePh\(_2\))Cl. Similar analogues, Co(CO)\(_3\)(PEt\(_3\))Cl and Co(CO)\(_3\)(PEt\(_3\))I were previously reported to display a strong \(\nu\)(CO) band at 1977 and 1976 cm\(^{-1}\) respectively previously. Using various concentrations of DCE added to benzene the quantum yield for the disappearance of Co\(_2\)(CO)\(_6\)(PMePh\(_2\))\(_2\) followed by formation of Co(CO)\(_3\)(PMePh\(_2\))Cl upon irradiation was determined. The \(\Phi\) values showed increased generation of the chlorinated photoproduct with increasing DCE concentration. This dependence of quantum yield on [DCE] is consistent with the photochemical homolytic cleavage of Co\(_2\)(CO)\(_6\)(PMePh\(_2\))\(_2\) to give the radical \(\cdot\text{Co(CO)}\(_3\)(PMePh\(_2\)). This radical is expected to either react competitively by a second order recombination to give the parent carbonyl or with excess DCE by a pseudo first order pathway to give the mononuclear chlorinated species. The results obtained by Ford and co-workers are in agreement with previous studies that show dinuclear complexes can undergo both ligand labialisation and metal-metal bond homolysis when irradiated.\(^\text{30}\)

\[\text{Co}_2\text{(CO)}_6\text{(PMePh}_2\text{)}_2 \xrightarrow{hv = 365 \text{ nm}} [\text{Co}_2\text{(CO)}_6\text{(PMePh}_2\text{)}_2]^* \]

\[2 \cdot\text{Co(CO)}\(_3\)(PMePh\(_2\)) \xrightarrow{\text{DCE}} \text{Co(CO)}\(_3\)(PMePh\(_2\))\text{Cl} \]

\(\text{Scheme 3} \quad \text{Photochemical pathways following irradiation of } \text{Co}_2\text{(CO)}_6\text{(PMePh}_2\text{)}_2 \text{ in DCE.}\)

Flash photolysis studies were carried out (1) under argon, (2) under CO and (3) under argon with an excess of PMePh\(_2\), to further investigate photochemical pathways and obtain kinetic data. (1) Flash photolysis of Co\(_2\)(CO)\(_6\)(PMePh\(_2\))\(_2\) in C\(_6\)D\(_6\) under argon (\(\lambda\)\(_\text{exc} = 308\) and 355 nm) resulted in bleaching of the parent carbonyl bands with simultaneous growth of a major product peak centred at 1940 cm\(^{-1}\), 12 cm\(^{-1}\) lower than to the parent absorbance at 1952 cm\(^{-1}\). The magnitude of the bleach of Co\(_2\)(CO)\(_6\)(PMePh\(_2\))\(_2\) was comparable for 308
and 355 nm photolysis however the absorbance at 1940 cm\(^{-1}\) was considerably larger in magnitude following 355 nm photolysis indicating that different photolysis wavelengths gave rise to different intermediates or else a different distribution of photoproducts. Kinetic traces of the changes in absorbance suggested that two photo processes occur. The faster process had a 2\(^{nd}\) order rate constant of 2 \(\times 10^7\) M\(^{-1}\) s\(^{-1}\) following 308 nm excitation and 8 \(\times 10^7\) M\(^{-1}\) s\(^{-1}\) following 355 nm excitation, while the slower process had a higher rate constant (9.6 \(\times 10^5\) M\(^{-1}\) s\(^{-1}\)) following 308 nm irradiation compared to (2.4 \(\times 10^5\) M\(^{-1}\) s\(^{-1}\)) 355 nm irradiation. This indicated the slower process was preferentially preformed on 308 nm excitation. This was in keeping with other polynuclear metal carbonyl studies,\(^{31}\) where CO photodissociation occurred preferentially following shorter wavelength irradiation. (2) Flash photolysis of Co\(_2\)(CO)\(_6\)(PMePh\(_2\))\(_2\) in C\(_6\)D\(_6\) under a CO atmosphere (\(\lambda_{\text{exc}} = 308\) and 355 nm) also resulted in bleaching of the parent absorbance at 1952 cm\(^{-1}\) with concomitant growth of a product band at 1939 cm\(^{-1}\). Analysis of the transient decay of the absorbance at 1939 cm\(^{-1}\), following 308 nm irradiation, \textit{via} a double exponential fit, indicated that two photoprocesses occur which both absorb at 1940 cm\(^{-1}\) and both react with free CO. The faster component with a second order rate constant (2.6 \(\times 10^6\) M\(^{-1}\) s\(^{-1}\)) was ascribed to the CO loss product Co\(_2\)(CO)\(_5\)(PMePh\(_2\))\(_2\) reacting with CO to reform the parent species. The slower component with a second order rate constant (1.5 \(\times 10^5\) M\(^{-1}\) s\(^{-1}\)) was ascribed to the reaction of the photogenerated radical species ·Co(CO)\(_3\)(PMePh\(_2\)) with CO \textit{via} ligand dissociation to form Co(CO)\(_4\). (3) Following photolysis of Co\(_2\)(CO)\(_6\)(PMePh\(_2\))\(_2\) in C\(_6\)D\(_6\) (\(\lambda_{\text{exc}} = 308\) nm) with added PMePh\(_2\) three temporal processes were observed. An immediate bleach at 1950 cm\(^{-1}\) corresponded to the photolytic depletion of the parent carbonyl complex owing to primary photochemistry, a continued absorbance decrease at 1950 cm\(^{-1}\) due to the decay of transient species and a slow increase in absorbance attributed to formation of Co\(_2\)(CO)\(_5\)(PMePh\(_2\))\(_3\). The absorbance at 1940 cm\(^{-1}\) which corresponded to the intermediates Co\(_2\)(CO)\(_5\)(PMePh\(_2\))\(_2\) and ·Co(CO)\(_3\)(PMePh\(_2\)) appeared then decayed below baseline as both transient species reacted with PMePh\(_2\) according to (pseudo) first order kinetics. The reaction of Co\(_2\)(CO)\(_5\)(PMePh\(_2\))\(_2\) to produce Co\(_2\)(CO)\(_5\)(PMePh\(_2\))\(_3\) had a rate constant of 3.9 \(\times 10^7\) M\(^{-1}\) s\(^{-1}\).
3.1.6 Pauson – Khand Reaction

The compounds produced from the reaction of alkynes with transition metals have found wide ranging uses but none more so than those of the type \((\mu_{2}\text{alkyne})\text{Co}_2(\text{CO})_6\) as they are important precursors in the formation of derivatised cyclopentanones. Metal-mediated co-cyclisation reactions have become more widely used in recent years especially since the discovery of the Pauson – Khand reaction (PKR).\(^{32}\) The products of the PKR can be highly regio- and stereo-chemically pure and as such are invaluable synthetic intermediates in a number of natural products syntheses, the synthesis of biologically important compounds such as prostaglandins,\(^{33}\) hirsutic acid\(^{34}\) and trans-dihydrojasmonate\(^{35}\) being just three examples.

The Pauson – Khand reaction represents the formal \([2 + 2 + 1]\) cycloaddition involving an alkene, alkyne and carbon monoxide to produce derivatised cyclopentanones and represents one of the most convergent methods in the synthesis of such compounds. Although the exact mechanism of the PKR has yet to be elucidated, a chemically reasonable pathway was proposed by Magnus\(^{36}\) and then by Schore,\(^{37}\) in which the initially formed \((\mu\text{-alkyne})\text{dicobalt hexacarbonyl cluster (d, Scheme 4)}\) loses a carbonyl ligand to form the pentacarbonyl cluster \((e, \text{Scheme 4})\) which provides an empty coordination site for alkene coordination \((f-1, f-2, \text{Scheme 4})\). It has been observed that the coordinating alkene positions itself closest to the least sterically bulky acetylenic substituent and that C-C bond formation occurs between this acetylenic carbon and the alkene. This results in the majority of cyclopentanones with the bulky acetylenic substituent in \(\alpha\) position on the compound, next to the C=O bond. Subsequent coupling of the alkyne and alkene to form the metallocycle \((g, \text{Scheme 4})\), alkyl migration to incorporate the carbonyl moiety and reductive elimination of the cyclopentanone form the final product \((i, \text{Scheme 4})\).
There are several disadvantages for the large scale commercial use of the classical PKR, namely the requirement for stoichiometric quantities of carbon monoxide (usually supplied by $\text{Co}_2(\text{CO})_8$) and the high reaction temperature required. Several studies have been carried out in order to develop systems which use only catalytic quantities of the metal carbonyl compound and/or use light to prompt the chemical reaction. Metal carbonyl complexes undergo photoinduced CO dissociation and Livinghouse et al. used high-intensity visible light to facilitate catalytic Pauson-Khand reactions. The purity of the dicobalt octacarbonyl catalyst and the choice of appropriate light source were found to be critical. Of those examined the Q-Beam light source proved most effective with a $\text{Co}_2(\text{CO})_8$ concentration of 5% providing the highest yields. Solvents including 1,2-dimethoxyethane (1,2-DME), ethyl acetate and diglyme also resulted in efficient conversion to the cyclopentanone. Thus under mild conditions (50 – 55 °C) and 1 atm CO the photochemically driven PKR can proceed.

In order to aid elucidation of the mechanism of the photo-induced PKR, the photochemistry of phenylacetylene dicobalt hexacarbonyl, ($\mu_2$-PhC≡CH)$\text{Co}_2(\text{CO})_6$, was
examined by matrix isolation techniques in conjunction with infra-red spectroscopy.\textsuperscript{40} Irradiation of \((\mu_2-\text{PhC}≡\text{CH})\text{Co}_2(\text{CO})_6\) isolated in an argon matrix with \(\lambda = 254\) nm resulted in depletion of the parent \(\nu(\text{CO})\) stretches and formation of the coordinately unsaturated \((\mu_2-\text{PhC}≡\text{CH})\text{Co}_2(\text{CO})_5\) species (“e” type species, Scheme 4). A photostationary state was reached upon conversion of 25\% of the starting material. No evidence was observed for the formation of a tetracarbonyl species, even on extended irradiation. Broadband photolysis at \(> 400\) nm regenerated the parent species although complete photoreversal could not be achieved. In an argon matrix doped with 10\% dinitrogen, irradiation at 254 nm resulted in the increased appearance of photoproducts with a greater amount of parent band depletion, indicative of a higher yielding photoreaction. The major photoproduct, the \(\text{N}_2\) coordinated pentacarbonyl species \((\mu_2-\text{PhC}≡\text{CH})\text{Co}_2(\text{CO})_5\text{N}_2\), was observed as the appearance of new carbonyl stretches in the IR spectrum, along with a number of unknown species formed. Continued photolysis at 390 nm resulted in the coordinately unsaturated \((\mu_2-\text{PhC}≡\text{CH})\text{Co}_2(\text{CO})_5\) species but had little effect on the \(\text{N}_2\) adduct. Broadband irradiation with \(\lambda > 400\) nm, as observed in the argon matrix, resulted in bleaching of the product bands with simultaneous regeneration of the parent bands. Irradiation of \((\mu_2-\text{PhC}≡\text{CH})\text{Co}_2(\text{CO})_6\) in a 100\% nitrogen matrix using \(\lambda = 254\) nm resulted in the rapid formation of the coordinated \(\text{N}_2\) pentacarbonyl species. Generation of a second \(\nu(\text{NN})\) band suggested the formation of a second \(\text{N}_2\) coordinated photoproduct. Once again broadband irradiation at \(\lambda > 400\) nm regenerated the parent species. Thus it was shown that the yield and rate of the pentacarbonyl formation increased as the \(\text{N}_2\) matrix gas concentration increased. In pure argon matrices in-cage recombination of the photoejected CO with the pentacarbonyl species occurred readily. Also irradiation at 350 nm of the parent species \((\mu_2-\text{PhC}≡\text{CH})\text{Co}_2(\text{CO})_6\) had little effect; it appeared to be photochemically inert at this wavelength.

It is widely accepted that decarbonylation (d → e, Scheme 4) of an initially formed \((\mu_2-\text{alkyne})\text{Co}_2(\text{CO})_6\) species is the precondition to the overall Pauson – Khand reaction sequence. The photochemical properties of these important intermediates in the PKR were examined by Long and co-workers by both steady state and laser flash photolysis.\textsuperscript{41} Generally these alkynyl dicobalt carbonyl compounds absorb across a broad range of wavelengths up to 630 nm providing a large choice of excitation wavelengths. Steady state photolysis of \((\mu_2-\text{PhC}≡\text{CH})\text{Co}_2(\text{CO})_6\) with \(\lambda_{\text{exc}} > 340\) nm, in the presence of a trapping ligand \((L = \text{PPh}_3\) or \(\text{C}_5\text{H}_5\text{N})\), produced the monosubstituted species, \((\mu_2-\text{PhC}≡\text{CH})\text{Co}_2(\text{CO})_5\text{L}\).
PhC=CHCo₂(CO)₅(L) with prolonged photolysis resulting in the disubstituted species (μ₂-PhC≡CH)Co₂(CO)₄(L)₂. Irradiation with λₑₓᶜ > 400 nm produced the same photoproducts although longer photolysis times were required. These results clearly showed that CO loss occurred via photochemical conditions, and the authors further investigated the process using monochromatic light sources. Laser flash photolysis of (μ₂-RC₂H)Co₂(CO)₆ (R = C₆H₅ or H) in cyclohexane solution was carried out. Pulsed photolysis (λₑₓᶜ > 355 nm) resulted in depletion of the parent hexacarbonyl absorbances within the rise-time of the monitoring beam (~20 ns) followed by a rapid recovery to the pre-irradiation levels. No transient absorbance signals were detected as far out as 600 nm. The kinetics of the recovery to pre-irradiation absorbance levels was found to be first order with a rate constant of 4 x 10⁷ s⁻¹ at 298 K. The rate of recovery of the depleted absorbance was unaffected following the addition of CO to the solution which suggested that the depletion of the parent absorbance was not a result of CO loss. Experiments using pyridine as a trapping ligand in 20-fold excess with the parent hexacarbonyl compound produced spectral changes showing the depletion of the parent carbonyl that recovered with an identical rate constant to that measured in the presence of CO, indicating that the intermediate produced did not react with pyridine. No photochemistry occurred from irradiation with λₑₓᶜ > 355 nm, which was in keeping with the results of Gordon et al.¹⁰ suggesting that (μ₂-C₆H₅C₂H)Co₂(CO)₆ is not CO substitution labile at this wavelength. The spectral changes were attributed to homolytic cleavage of the cobalt – cobalt bond (Scheme 5), which rapidly underwent efficient recombination resulting in no permanent or long lived bleaching. However, pulsed photolysis with λₑₓᶜ > 532 nm produced a transient species that absorbed with a λₑₓᶜ at 400 nm that was assigned to the pentacarbonyl species. Typical of the reaction of CO loss intermediates, addition of CO reduced the lifetime of the transient species although its yield remained unaffected. The observed rate constant, kₑₓᶜ, was found to be linearly dependent on the concentration of CO, with a second order rate constant of 1.2 x 10⁶ M⁻¹ s⁻¹ (298 K). In the presence of excess triphenylphosphine, irradiation produced a transient at 400 nm assigned to the pentacarbonyl species (μ₂-RC₂H)Co₂(CO)₅(PPh₃) (Scheme 5). The lifetime and yield of the transient species depended on the concentration of the PPh₃, as was the case in CO addition. The second order rate constant for the substitution was found to be 3 x 10⁶ M⁻¹ s⁻¹ at 298 K.
The factors influencing the regio-chemical outcome of the PKR were examined using theoretical methods. In the vast majority of reactions, the larger acetylenic moiety was found at the α position in the resulting pentanone. The authors postulate that the regio-chemistry of the reaction is governed, through the discriminate loss of a CO, almost exclusively by the electronic nature of the acetylenic substituents. Numerous studies have indicated that the nature of these substituents can affect the electronic properties within the ($\mu_2$-alkyne)Co$_2$(CO)$_6$ complex. $^{13}$Carbon NMR analysis of the CO carbons in ($\mu_2$-RC≡CR‘)Co$_2$(CO)$_6$ indicate that they are affected by the nature of the R/R’ groups. An increase in the electron donating ability of the R groups causes downfield shifts of the CO resonances. Infra-red spectroscopy has also shown that the ν(CO) stretches in the carbonyl region of the spectrum shift as a function of R/R’ substituents. Increasing the electronegativity of R/R’ causes an increase in the vibrational frequencies observed. The difference in electron density on the two acetylenic carbons in the complex may be

\textit{Scheme 5} Observed wavelength dependent photochemistry of $(\mu_2$-RC$_2$H$_2$)Co$_2$(CO)$_6$ in cyclohexane solution, in the presence of either PPh$_3$ or pyridine.
responsible for the discriminate loss of CO. DFT calculations indicated that different substituents on the acetylene give rise to different electronic densities on its carbon atoms which results in polarisation of the alkyne bond. The electronic effects caused by the different substituents influence the position from which carbon monoxide is lost and ultimately the regio-chemistry of the reaction. It is assumed that the initial step of CO loss from the \( (\mu_2\text{-alkyne})\text{Co}_2(\text{CO})_6 \) provides a coordination site for the incoming alkene, the position of which fixes the regiochemistry of the resulting cyclopentanone adduct. In the case where the \( C_R \) of the acetylenic \( C_R-C_{R'} \) bond possesses the larger electron density, a longer Co-CO bond length is calculated for the carbon monoxides that are trans-positioned with respect to \( R' \). It is reasonable to expect that these CO ligands would dissociate more easily. A complex where the acetylenic \( C_R-C_{R'} \) bond lacks significant polarisation, the Co-CO bond lengths were found to be almost identical. The CO ligands should dissociate with equal facility and therefore steric effects as opposed to electronic effects become the determining factor. Finally in the case where the acetylene substituents are sterically virtually identical but electronically different the result was found to be the same. The \( C_{R'} \) of the \( C_R-C_{R'} \) polarised bond had the higher electron density and resulted in the carbon monoxides that are cis-positioned with respect to the dissociating \( R \) group. This provides an alternative to the “steric rationale” for mechanistic interpretation of the PKR.

Recently, a series of \( (\mu_2\text{-alkyne})\text{Co}_2(\text{CO})_5(\eta^2\text{-alkene}) \) complexes have been reported and as such are the first isolated examples in the next step of the PKR.\(^{38}\) A range of 5-alkynyl-5\( H \)-dibenzo[\( a,d \)]cycloheptenes (77 – 82A, Fig. 15) were allowed to react with dicobalt octacarbonyl and two products were isolated: the major product (57 – 88 %) was the anticipated hexacarbonyl cluster (77 – 82B, Fig. 15) and the minor product (6.5 – 16 %) was the pentacarbonyl complex (77 – 82C, Fig. 15). In the pentacarbonyl species the third ligand site on one of the cobalt centres is occupied by the double bond of the seven membered ring. The thermal instability of the hexacarbonyl clusters and therefore the facile reaction to form the pentacarbonyl complex was surprising, decarbonylation of the hexacarbonyl and formation of the pentacarbonyl complex occurred in solution at room temperature. The authors suggested that CO loss was compensated for by formation of the cobalt-alkene complex as a chelate. Several theoretical studies calculated geometries for the incoming ethylene and found it favours a pseudoaxial site such that the distance between an alkene carbon and the nearer alkyne carbon is approximately 2.95 Å.
Crystallographic structures of ($\mu_2$-alkyne)Co$_2$(CO)$_5$(η$^2$-alkene) complexes (77 – 82C, Fig. 15) revealed carbon-alkene-carbon distances of 2.133 to 2.184 Å, with cobalt-complexes alkene carbons within 2.817 – 2.880 Å from the nearer alkyne carbon, somewhat shorter than expected. Despite the proximity of these carbons, the pentacarbonyl complexes were reasonably stable and the PKR did not continue to the corresponding cyclopentanones (77 – 82D, Fig. 15). The authors postulated that alkene insertion in this type of complex occurred preferentially from the equatorial position and the continuation of the PKR was precluded by severe ring strain caused by the rigidity of this class of compound (77 – 82C). The activation energy for the decarbonylation process was found to be ~29 kcal mol$^{-1}$ and the overall reaction was endothermic by ~14 kcal mol$^{-1}$. These values correlate very well with theoretically values calculated by Yamanaka and Nalamura$^{43}$ ($E_{\text{act}}$ and $\Delta H =$ 26.4 and 14.6 kcal mol$^{-1}$ respectively) and Pericàs et al.$^{44}$ ($E_{\text{act}}$ and $\Delta H =$ 33.5 and 12 kcal mol$^{-1}$ respectively) especially as their calculations are based on an intermolecular reaction to form ($\mu_2$-C$_2$H$_2$)Co$_2$(CO)$_5$(η$^2$-C$_3$H$_4$), whereas the experimental data were obtained for a more heavily substituted intramolecular process.

![Figure 15](image-url)  

**Figure 15** Isolated intermediates of the Pauson Khand reaction.$^{38}$
3.2 Abstract

The aim of this chapter is to investigate the photochemistry of simple aromatic molecules and corresponding dicobalt hexacarbonyl complexes. Central to elucidating photochemical processes in more sophisticated assemblies is a fuller understanding of the spectroscopy and photochemistry of simple aromatic and organometallic molecules. Developing a better grasp of the photochemistry of simple molecules will aid the enhancement of our ability to create and improve practical applications in photochemical processes. In this chapter a concerted experimental investigation into the photochemistry dicobalt carbonyl complexes was undertaken, focusing on the effects of terminal group substitution on the aromatic core and the primary photoactivation processes in Co-Co complexes.

Thienylacetylene systems have been extensively studied yet the affect of terminal group substitution in such systems less so. Rodríguez et al. focused on chain length in these systems and the influence of double bonds versus triple bonds was examined. Where the double bonds were replaced by a triple bond, an increase in fluorescence quantum yield was observed. Toyota et al. synthesised a series of compounds with a phenylene axis and a pair of thien-3-yl moieties at each end. The effect of substitution of the thiophene with ethynylTMS, ethynylbenzene and ethynylpyridine units was examined. Results indicated that the additional aryl groups increase the conjugation within the molecule and as a result the electronic properties were altered. Coleman et al. examined a series of pyrene-thiophene dyads. In all cases, luminescence from the pyrene chromophore was observed, which was reduced upon complexation with dicobalt hexacarbonyl. The luminescence of these compounds and complexes was affected by ligand substitution also. As discussed previously, experimental evidence for the accepted mechanism of the PKR has been limited. Long et al. carried out thorough investigations of dicobalt hexacarbonyl complexes. Two possible photochemical pathways were proposed for (μ2-alkyne)Co2(CO)6 complexes following excitation. Irradiation at λ_{exc} = 355 nm resulted in Co-Co bond homolysis with τ_{recomb} = 25 ns, while irradiation at λ_{exc} = 254 nm in an argon matrix resulted in reversible CO loss. More recently Gibson et al. reported that Co-Co cleavage competes with CO loss and alkene binding in an (alkyne)(binap)tetracarbonyl dicobalt complex and that the Co-Co bond cleavage was a facile process.
Thus, a series of simple organic thienylacetylene based molecules were synthesised, along with their corresponding dicobalt hexacarbonyl complexes (Fig. 16). Ligands, **NB-L1 – NB-L4**, were examined to delineate the effect of a thiophene moiety attached in the thien-2-yl or thien-3-yl position. While ligands, **NB-L1** and **NB-L5 – NB-L8**, can be used to investigate the effect of terminal group substitution on the organic moiety, with respect to their absorbance, emission and electrochemistry. A previously reported investigation into the photochemistry of diphenylacetylene revealed that it was a non fluorescent molecule which became weakly fluorescent when a terminal electron withdrawing group was attached. This too was investigated for the thienylacetylene systems by steady state fluorescence techniques.

For the dicobalt hexacarbonyl complexes, the two competing routes of CO loss and Co-Co bond homolysis were investigated by various methods. Steady state photolysis and quantum yield measurements of CO loss was be carried out in order to examine whether CO loss occurred from these complexes and with what efficiency. TRIR spectroscopy with ps resolution will aid the identification of the primary photoprocesses that occur on a picosecond timescale following excitation.

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**Figure 16**  Complexes synthesised for the investigation in chapter 3
A shift in the absorbance and emission maxima in the spectra of the thienylacetylene molecules is expected were appropriate substitution has occurred. It is expected that the more electronegative the terminal substituent the greater the spectral changes will be. The non fluorescent molecules may become weakly fluorescent upon appropriate terminal group substitution as was observed for diphenylacetylene.

For the dicobalt hexacarbonyl complexes, steady state photolysis in the presence of a trapping ligand is expected to result in CO loss as this has been observed for similar systems. The extent of CO loss may be substituent dependant, which will be revealed by the quantum yield measurements. To date, TRIR has not been used to investigate the photochemistry of (µ2-alkyne)Co₂(CO)₆ type complexes. Thus, picosecond time resolved infrared spectroscopy was used to probe the photochemistry of three (µ2-alkyne)Co₂(CO)₆ complexes. The results from TRIR spectroscopy will hopefully reveal what initial photoprocess occur following excitation (CO loss or Co-Co bond homolysis) and aid in the indentification of transient species formed. This is of particular interest as it relates to the initiation of the well known PKR.
3.3 Experimental

3.3.1 Materials

Any experiments that required an inert atmosphere were carried out under argon or nitrogen using standard Schlenk techniques. All solvents were supplied by the Aldrich Chemical Company. Dichloromethane, chloroform, diethyl ether, pentane and hexane were dried over MgSO$_4$ prior to use. Tetrahydrofuran (THF) was distilled from sodium / benzophenone solution and used immediately. Anhydrous triethylamine was used as received and diisopropylamine was distilled over potassium hydroxide prior to use. All organic reagents were purchased from the Aldrich Chemical Company. Diphenylacetylene and ethynylferrocene were used as received. 5-Bromothiophene-2-carboxaldehyde was purified by distillation using a Buchi Kügelrohr apparatus. All mobile phases for column chromatography were dried over MgSO$_4$ and silica gel (Merck) was used as received. All solvents used in absorbance, emission, lifetime and quantum yield experiments were of spectroscopic grade and used without further purification. All solvents were deoxygenated by purging with pure argon or nitrogen for ~10 minutes. The preface “NB-” is applied to compound codes indicating that these are novel compounds synthesised throughout this work.

3.3.2 Equipment

All syntheses involving air- and moisture-sensitive reagents were performed in oven or flame dried glassware. NMR spectra were recorded on a Bruker model AC 400 MHz spectrometer and Bruker model ANC 600 MHz spectrometer using CDCl$_3$ as solvent. All NMR spectra were calibrated according to the residual solvent peak, i.e. CHCl$_3$ at 7.26 ppm for all $^1$H spectra and 77.16 ppm for all $^{13}$C spectra. Chemical shifts ($\delta$) are given in parts per million (ppm). Proton coupling constants ($J$) are given in Hertz (Hz). Melting points were measured on a Stuart Scientific SMP1 melting point apparatus. All UV-vis spectra were measured on an Agilent Technologies 8453 photodiode array spectrometer using a 1 cm$^3$ quartz cell. Emission spectra (accuracy $\pm$ 5 nm) were recorded at 298 K using a LS50B luminescence spectrophotometer, equipped with a red sensitive Hamamatsu R928 PMT detector, interfaced with Elonex PC466 employing Perkin-Elmer FL WinLab custom built software. Luminescence lifetime measurements were made using an
Edinburgh Analytical Instruments (EAI) Time-Correlated Single Photon Counting apparatus (TCSPC) as described by Browne et al.\textsuperscript{46} IR spectra were recorded on a Perkin-Elmer 2000 FT-IR spectrometer (2 cm\textsuperscript{-1} resolution) in a 0.1 mm sodium chloride liquid solution cell. Cyclic voltammetry experiments were carried out using a CH instruments model 600a electrochemical workstation at a scan rate of 0.1 VS\textsuperscript{-1}. Electrochemical studies were conducted using a three electrode system with 0.1 M solution of TBAPF\textsubscript{6} in anhydrous acetonitrile as supporting electrolyte. The working electrode was a 3 mm diameter Teflon shrouded platinum electrode, which was polished before each use. The counter electrode was a platinum wire and the reference electrode was a non-aqueous Ag/Ag\textsuperscript{+} electrode. Deoxygenation of the solutions was achieved by bubbling through argon for approximately 10 minutes and a blanket of argon was maintained over the solution during all experiments. The filling solution for the Ag/Ag\textsuperscript{+} reference electrode was 0.1 M TBAPF\textsubscript{6} and 10 mM AgNO\textsubscript{3} in anhydrous acetonitrile. All potentials are quoted with respect to the potentials of the ferrocene/ferricenium couple ($E^\circ' = 0.382$ V vs. SCE).
3.3.3 Synthesis

Procedure for the preparation of compounds via the Sonogashira reaction.\(^1\)

To a flame dried round bottom flask anhydrous triethylamine (∼30 ml) was added and purged with nitrogen for 10 minutes. Following this, the appropriately substituted halogenated thiophene was added and the solution was purged for a further 5 minutes. A catalytic quantity of bis(triphenylphosphine)palladium(II)chloride, triphenylphosphate and cuprous iodide were added to the flask followed by an excess of aryl alkyne in quick succession. The reaction mixture was refluxed overnight under an inert atmosphere and then allowed to cool. Excess aryl and solvent was removed under reduced pressure. The crude product was extracted from the brown oil by first adding ca. 5 ml of dichloromethane followed by the addition of ca. 25 ml of petroleum ether (or hexane). The solvent layer was then decanted off. This process was repeated several times until the washings remained colourless. The washings were combined and dried over magnesium sulphate. The solvent was then removed via rotary evaporation affording a dark viscous oil. The crude product was then purified using a Kügelrohr or by column chromatography as described for each compound.

Procedure for the preparation of dicobalt hexacarbonyl complexes.

To a flame dried round bottom flask hexane was added and purged with nitrogen for 10 minutes. Molar equivalents of the relevant substituted ethynylthiophene ligand and Co\(_2\)(CO)\(_8\) (in some cases an excess of the metal carbonyl was used) were added to the reaction vessel which was then covered in tin foil. This solution was stirred overnight at room temperature under inert conditions and to yield a dark brown solution. The crude product was subsequently purified by column chromatography on silica gel using a mobile phase of hexane (100 %) then increasing the polarity (as stated or individual compounds) to elute the desired product band.
3.3.3.1 2-(Phenylethynyl)thiophene (NB-L1)

![Chemical structure of 2-(Phenylethynyl)thiophene (NB-L1)]

2-Bromothiophene (3.0 mmol, 0.29 ml), bis(triphenylphosphine) palladium(II)chloride (0.06 mmol, 42 mg, 2 %), triphenylphosphine (0.12 mmol, 31 mg, 4%), cuprous iodide (0.06 mmol, 11 mg, 2 %) and 1-phenylacetylene (5.7 mmol, 0.63 ml) were used. The crude product was purified using a Kügelrohr (240 °C, 0.04 mm Hg) which afforded a white solid. Yield: 502 mg, 2.72 mmol, 91 %. Spectroscopic data were in good agreement with reported data.\(^{47}\)

\(^{1}\)H NMR (600 MHz, CDCl\(_3\)): 7.53 – 7.51 (2H, m), 7.38 – 7.33 (3H, m), 7.30 – 7.29 (2H, m), 7.02 – 7.01 (1H, m) ppm. \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): 131.91, 131.44, 128.45, 128.39, 127.27, 127.12, 123.36, 122.96, 93.04, 82.63 ppm. \(\text{m.p.} = 51 – 52^\circ\text{C}\).
3.3.3.2 3-(Phenylethynyl)thiophene (NB-L2)

\[
\begin{align*}
\text{Br} & \quad \text{S} \\
\text{HC≡} & \quad \text{Et}_3\text{N} / \Delta / \text{N}_2 \\
2 \% \text{Pd} & \quad (\text{PPh}_3)_2\text{Cl}_2 \\
2 \% \text{CuI} & \\
4 \% \text{PPh}_3 \\
\text{S} & \quad \text{Et}_3\text{N} / \Delta / \text{N}_2 \\
2 \% \text{Pd} & \quad (\text{PPh}_3)_2\text{Cl}_2 \\
2 \% \text{CuI} & \\
4 \% \text{PPh}_3
\end{align*}
\]

3-Bromothiophene (3.0 mmol, 0.28 ml), bis(triphenylphosphine) palladium(II)chloride (0.06 mmol, 42 mg, 2 %), triphenylphosphine (0.12 mmol, 31 mg, 4%), cuprous iodide (0.06 mmol, 11 mg, 2 %) and 1-phenylacetylene (5.7 mmol, 0.63 ml) were used. The crude product purified using a Kugelrohr (225 °C, 0.04 mm Hg) which afforded an off white solid. Yield: 447 mg, 2.43 mmol, 81 %. Spectroscopic data were in good agreement with reported data.48

\(^1\text{H NMR}\) (600 MHz, CDCl\(_3\)): 7.52 – 7.51 (3H, m), 7.35 (1H, s), 7.34 – 7.32 (2H, m), 7.31 – 7.29 (1H, m), 7.21 – 7.19 (1H, m) ppm. \(^{13}\text{C NMR}\) (150 MHz, CDCl\(_3\)): 131.55, 129.90, 128.60, 128.35, 128.22, 125.37, 123.24, 122.35, 88.91, 84.52 ppm. \text{m.p.:} = 34-35 °C.
2-Bromothiophene (4.0 mmol, 0.38 ml), bis(triphenylphosphine)palladium(II)chloride (0.06 mmol, 42 mg, 2 %), triphenylphosphine (0.12 mmol, 31 mg, 4%), cuprous iodide (0.06 mmol, 11 mg, 2 %) and 2-ethynylthiophene (3.0 mmol, 0.30 ml) were used. The crude product was purified by careful Kügelrohr distillation (115 ºC, 0.04 mm Hg) affording an off white solid. Yield: 427 mg, 2.24 mmol, 75 %. Spectroscopic data were in good agreement with reported data.\textsuperscript{49}

\textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}): 7.30 (2H, d, \textit{J} = 6 Hz), 7.28 (2H, d, \textit{J} = 6 Hz), 7.01 (2H, t, \textit{J} = 6 Hz). \textsuperscript{13}C NMR (150 MHz, CDCl\textsubscript{3}): 132.14, 127.66, 127.14, 122.95, 86.20 ppm. \textbf{m.p.}: 94-95 ºC.
3.3.3.4 2-(Thien-3-ylethynyl)thiophene (NB-L4)

![Reaction scheme](image)

3-Bromothiophene (4.0 mmol, 0.38 ml), bis(triphenylphosphine)palladium(II)chloride (0.06 mmol, 42 mg, 2 %), triphenylphosphine (0.12 mmol, 31 mg, 4%), cuprous iodide (0.06 mmol, 11 mg, 2 %) and 2-ethynylthiophene (3.0 mmol, 0.30 ml) were used. The crude product purified using a Kügelrohr (125 ºC, 0.04 mm Hg) which afforded a cream coloured solid. Yield: 352 mg, 1.85 mmol, 62 %. Spectroscopic data were in good agreement with reported data.

**¹H NMR** (600 MHz, CDCl₃): 7.54-7.50 (1H, m), 7.31-7.30 (1H, m), 7.29-7.28 (1H, m), 7.27-7.26 (1H, m), 7.19-7.18 (1H, m), 7.01-7.09 (1H, m) ppm. **¹³C NMR** (150 MHz, CDCl₃): 132.17, 131.86, 129.73, 128.83, 127.21, 127.11, 125.49, 121.98, 88.21, 82.12 ppm. **IR** (CH₂Cl₂): (C≡C) 2203 cm⁻¹. **m.p.:** 88-89 ºC.
3.3.3.5 2-Iodo-5-bromothiophene

\[
\begin{array}{c}
\text{Br} \quad \text{S} \quad \text{I}_2 \quad \text{Acid} \quad \Delta \quad \text{Br} \quad \text{S} \quad \text{I}
\end{array}
\]

2-Iodo-5-bromothiophene was prepared in a similar manner to that described by Holmes et al.\(^\text{50}\) Initially a flame dried round bottom flask was charged with CH\(_2\)Cl\(_2\) (16 ml) and 2-bromothiophene (7.8 mmol, 0.76 ml) and purged with nitrogen for 10 minutes. Subsequently iodine (4.0 mmol, 1.0 g) was added followed by freshly prepared 8.5 M nitric acid (12 ml) (37.72 ml of conc. nitric acid in 100 ml H\(_2\)O). The reaction mixture was refluxed for six hours under an inert atmosphere. The reaction was quenched with water and the organic layer extracted with CH\(_2\)Cl\(_2\). The crude product was then washed with 50 % w/v aqueous sodium thiosulphate and dried over MgSO\(_4\). Excess solvent was removed under \textit{via} rotary evaporation. The crude product was then purified by careful Kügelrohr distillation (95 °C, 0.04 mm Hg) to give a colourless oil. Yield: 1.95 g, 6.75 mmol, 86 %. Spectroscopic data were in good agreement with reported data.\(^\text{50}\)

\(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)): 7.04 (1H, d, \(J = 3.6\) Hz), 6.75 (1H, d, \(J = 3.6\) Hz) ppm.

\(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)): 137.28, 131.51, 115.10, 72.52 ppm
3.3.3.6 2-(Phenylethynyl)-5-bromothiophene (NB-L5)

\[
\begin{align*}
\text{Br} & \quad \text{S} & \quad \text{I} \\
\text{Et}_3\text{N} / \Delta / \text{N}_2 & \quad 6 \% \text{Pd(PPh}_3\text{)}_2\text{Cl}_2 & \quad 6 \% \text{CuI} \\
& \quad 12 \% \text{PPh}_3
\end{align*}
\]

2-Bromo-5-iodothiophene (4.43 mmol, 1.28 g), bis(triphenylphosphine) palladium(II)chloride (0.27 mmol, 189 mg, 6 %), triphenylphosphine (0.54 mmol, 142 mg, 12 %), cuprous iodide (0.27 mmol, 51 mg, 6 %) and 1-phenylacetylene (5.7 mmol, 0.63 ml) were used. The crude product was purified using a Kügelrohr (150 ºC, 0.04 mm Hg) which afforded a white solid. Yield: 982 mg, 3.73 mmol, 83 %.

\[\text{H NMR} (600 \text{ MHz, CDCl}_3): 7.53 - 7.48 (2\text{H, m}), 7.38 - 7.32 (3\text{H, m}) 7.02 (1\text{H, d, } J = 4 \text{ Hz}), 6.96 (1\text{H, d, } J = 4 \text{ Hz}) \text{ ppm.} \]

\[\text{C NMR} (150 \text{ MHz, CDCl}_3): 131.46, 129.23, 128.72, 128.47, 128.44, 125.12, 122.54, 121.83, 94.06, 81.68 \text{ ppm. IR} (\text{CH}_2\text{Cl}_2): (\text{C≡C}) 2207 \text{ cm}^{-1}.\]

m.p.: 54-55 ºC.
3.3.3.7 2-(Phenylethynyl)thiophene-5-methylenemalononitrile (NB-L7)

The dicyanovinyl derivative, NB-L7, was synthesised via a Knoevenagel condensation reaction of 2-(phenylethynyl)thiophene-5-carboxaldehyde (synthesis of the aldehyde, NB-A1, described in chapter 2, page 101). Argon purged ethanol (40 ml) was charged with 5-(phenylethynyl)thiophene-2-carboxaldehyde (4.0 mmol, 850 mg), malonitrile (4.0 mmol, 0.25 ml) and 3-4 drops piperidine. This yellow solution was then heated to reflux for 1 hour under an inert atmosphere to yield a dark red solution. Solvent was removed under reduced pressure yielding a dark red-brown coloured solid. This residue was purified by column chromatography using silica gel and CH$_2$Cl$_2$ as mobile phase to yield a dark orange solid. Yield: 562 mg, 2.16 mmol, 54 %.

$^1$H NMR (400 MHz, CDCl$_3$): 7.77 (1H, s), 7.66 (1H, d, $J = 4$ Hz), 7.56 – 7.54 (2H, m), 7.43 – 7.37 (3H, m) 7.33 (1H, d, $J = 4$ Hz) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): 150.04, 138.55, 135.62, 134.98, 132.64, 131.80, 129.81, 128.67, 121.51, 113.84, 100.81, 81.70, 78.11 ppm. IR (CH$_2$Cl$_2$): (C=–C) 1576, (C≡C) 2203, (C≡N) 2226 cm$^{-1}$. m.p.: 137-138 °C.
2-(Phenylethynyl)-5-bromothiophene (2.28 mmol, 600 mg), bis(triphenylphosphine) palladium(II) chloride (0.05 mmol, 32 mg, 2%), triphenylphosphine (0.09 mmol, 24 mg, 4%), cuprous iodide (0.05 mmol, 9 mg, 2%) and 9-ethynylphenanthrene (3.0 mmol, 607 mg) were used. The crude product purified by careful column chromatography using silica gel and CH$_2$Cl$_2$ / hexane (40:60) as mobile phase affording a bright yellow solid. Yield: 726 mg, 1.89 mmol, 83%.

$^1$H NMR (400 MHz, CDCl$_3$): 8.72-8.70 (1H, m), 8.67 (1H, d, $J = 8$ Hz), 8.47-8.45 (1H, m), 8.09 (1H, s), 7.88 (1H, d, $J = 8$ Hz), 7.73-7.71 (2H, m), 7.70 – 7.67 (1H, m), 7.64-7.60 (1H, m), 7.56-7.52 (3H, m), 7.38-7.33 (4H, m), 7.29 (1H, d, $J = 4$ Hz), 7.22 (1H, d, $J = 4$ Hz) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): 131.47, 131.09, 131.02, 130.93, 130.48, 130.10, 129.73, 129.39, 129.06, 128.19, 127.69, 127.66, 127.42, 126.70, 126.21, 126.17, 126.04, 125.79, 123.88, 123.58, 121.83, 121.63, 121.54, 91.56, 85.67, 81.27 ppm. IR (CH$_2$Cl$_2$): (C≡C) 2201 cm$^{-1}$. m.p.: 150-151 ºC.
3.3.3.9 Diphenylacetylene dicobalt hexacarbonyl (PhCCPh-Co$_2$(CO)$_6$)

Diphenylacetylene (1.12 mmol, 200 mg) and Co$_2$(CO)$_8$ (1.12 mmol, 384 mg) were used. The crude product was purified by column chromatography using silica gel and hexane (100 %) as mobile phase which furnished the pure reddish-brown product. Yield: 483 mg, 1.04 mmol, 93 %. Spectroscopic data are in good agreement with reported data.\textsuperscript{51}

$^1$H NMR (400 MHz, CDCl$_3$): 7.61-7.60 (m, 2H) 7.59-7.58 (m, 2H), 7.39-7.37 (m, 3H), 7.35-7.33 (m, 3H) ppm. IR (CH$_2$Cl$_2$): $\nu$(CO) 2090, 2056, 2028 cm$^{-1}$. 

\begin{figure}
\centering
\includegraphics[width=\textwidth]{image}
\caption{Diphenylacetylene dicobalt hexacarbonyl (PhCCPh-Co$_2$(CO)$_6$)}
\end{figure}
3.3.3.10  2-(Phenylethynyl)thiophene dicobalt hexacarbonyl (NB-C1)

\[
\begin{align*}
\text{Hexane} & \quad \text{N}_2 / \text{R.T.} \\
\end{align*}
\]

2-(Phenylethynyl)thiophene (1.08 mmol, 200 mg) and \( \text{Co}_2(\text{CO})_8 \) (1.08 mmol, 370 mg) were used. The crude product was purified by column chromatography using silica gel and hexane : \( \text{CH}_2\text{Cl}_2 \) (70 : 30) as mobile phase which furnished the pure reddish-brown product. Yield: 457 mg, 0.97 mmol, 90 %

\(^1\text{H NMR}\) (600 MHz, CDCl\(_3\)): 7.70-7.68 (2H, m), 7.42-7.35 (5H, m), 7.06-7.04 (1H, m) ppm. \(^{13}\text{C NMR}\) (150 MHz, CDCl\(_3\)): 198.57, 141.57, 137.23, 137.64, 128.92, 128.73, 128.37, 127.88, 126.70, 91.58, 82.04 ppm. \( \text{IR} \) (\( \text{CH}_2\text{Cl}_2 \)): \( \nu(\text{CO}) \) 2091, 2058, 2030 cm\(^{-1}\).
3.3.3.11 3-(Phenylethynyl)thiophene dicobalt hexacarbonyl (NB-C2)

3-(Phenylethynyl)thiophene (1.63 mmol, 300 mg) and Co$_2$(CO)$_8$ (1.63 mmol, 557 mg) were used. The crude product was purified by column chromatography using silica gel and hexane : CH$_2$Cl$_2$ (70 : 30) as mobile phase, which furnished the pure reddish-brown product. Yield: 568 mg, 1.21 mmol, 74 %.

$^1$H NMR (400 MHz, CDCl$_3$): 7.62-7.60 (3H, m), 7.52-7.49 (3H, m), 7.34-7.32 (1H, m), 7.25-7.24 (1H, m) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): 198.3, 137.20, 130.50, 128.84, 128.16, 127.96, 127.36, 125.50, 122.71, 87.90, 83.40 ppm. IR (CH$_2$Cl$_2$): ν(CO) 2090, 2055, 2028 cm$^{-1}$. 

![Chemical structure of 3-(Phenylethynyl)thiophene dicobalt hexacarbonyl](image-url)
2-(Thien-2-ylythynyl)thiophene (0.82 mmol, 157 mg) and Co$_2$(CO)$_8$ (0.90 mmol, 308 mg) were used. The crude product was purified by column chromatography using silica gel and a mobile phase of hexane (100 %) followed by hexane : CH$_2$Cl$_2$ (70 : 30) which furnished the pure reddish-brown product. Yield: 333 mg, 0.70 mmol, 85 %

$^1$H NMR (400 MHz, CDCl$_3$): 7.42-7.41 (2H, m), 7.40-7.38 (2H, m), 7.06-7.03 (2H, m) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): 197.70, 140.40, 128.79, 127.01, 126.13, 81.12 ppm.

IR (CH$_2$Cl$_2$): $\nu$(CO) 2091, 2058, 2031 cm$^{-1}$. 

3.3.3.12 2-(Thien-2-ylythynyl)thiophene dicobalt hexacarbonyl (NB-C3)
3.3.3.13 2-(Thien-3-ylethenyl)thiophene dicobalt hexacarbonyl (NB-C4)

![reaction_diagram]

2-(Thien-3-ylethenyl)thiophene (0.66 mmol, 126 mg) and Co₂(CO)₈ (0.66 mmol, 226 mg) were used. The crude product was purified by column chromatography using silica gel and a mobile phase of hexane (100 %) followed by hexane : CH₂Cl₂ (70 : 30) which furnished the pure reddish-brown product. Yield: 247 mg, 0.52 mmol, 79 %.

¹H NMR (600 MHz, CDCl₃): 7.68-7.65 (1H, m), 7.45-7.33 (3H, m), 7.20-7.18 (1H, m), 7.05-7.01 (1H, m) ppm. ¹³C NMR (150 MHz, CDCl₃): 198.57, 132.12, 131.39, 131.03, 130.05, 129.07, 128.65, 128.37, 125.05, 93.99, 81.63 ppm. IR (CH₂Cl₂): ν(CO) 2091, 2059, 2032 cm⁻¹.
2-(Phenylethynyl)-5-bromothiophene (0.49 mmol, 128 mg) and Co$_2$(CO)$_8$ (0.54 mmol, 185 mg) were used. The crude product was purified by column chromatography using silica gel and a mobile phase of hexane (100 %) which furnished the pure reddish-brown product. Yield: 242 mg, 0.44 mmol, 90 %.

$^1$H NMR (400 MHz, CDCl$_3$): 7.64-7.50 (3H, m), 7.40-7.30 (2H, m), 7.05-7.01 (2H, m) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): 198.76, 137.89, 131.67, 129.50, 128.63, 128.06, 126.95, 126.67, 123.72, 88.08, 81.96 ppm. IR (CH$_2$Cl$_2$): ν(CO) 2092, 2057, 2030 cm$^{-1}$. 
2-(Phenylethynyl)thiophene-5-carboxaldehyde (1.41 mmol, 300 mg) and Co$_2$(CO)$_8$ (1.55 mmol, 530 mg) were used. The crude product was purified by column chromatography using silica gel and a mobile phase of hexane (100 %) followed by hexane : diethyl ether (60 : 40) which furnished the pure reddish-brown product. Yield: 492 mg, 0.99 mmol, 70 %.

$^1$H NMR (400 MHz, CDCl$_3$): 9.88 (1H, s), 7.69-7.68 (1H, m), 7.63-7.62 (2H, m), 7.39-7.36 (4H, m) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): 198.25, 182.50, 153.74, 143.23, 137.28, 137.15, 129.17, 128.89, 128.49, 92.64, 79.40 ppm. IR (CH$_2$Cl$_2$): ʋ(C=O) 1652, ʋ(M-CO) 2095, 2062, 2035 cm$^{-1}$.  

\[
\text{Co}_2(\text{CO})_8 \quad \text{Hexane} \quad \text{N}_2 / \text{R.T.} \quad \text{Co}_2(\text{CO})_6
\]
2-(Phenylethynyl)thiophene-5-methylenemalononitrile (0.48 mmol, 125 mg) and Co$_2$(CO)$_8$ (0.58 mmol, 198 mg) were used. To aid dissolution of the dicyanovinyl ligand THF (3 ml) was also used. The crude product was purified by column chromatography using silica gel and a mobile phase of hexane (100%) followed by hexane : diethyl ether (3 : 2) which furnished the pure reddish-brown product. Yield: 109 mg, 0.20 mmol, 42%

$^1$H NMR (600 MHz, CDCl$_3$): 7.75 (1H, s), 7.64-7.56 (3H, m), 7.49-7.35 (3H, m), 7.29-7.27 (1H, m) ppm. $^{13}$C NMR (150 MHz, CDCl$_3$): 198.89, 152.47, 141.54, 137.23, 137.01, 132.86, 131.82, 128.93, 128.64, 126.33, 114.26, 105.56, 81.35, 79.75 ppm. IR (CH$_2$Cl$_2$): ν(CO) 2094, 2061, 2034 (C≡C) 1576, (C≡N) 2226 cm$^{-1}$
3.3.3.17 2-(Phenylethynyl)thiophene-5-ethynylphenanthrene dicobalt hexacarbonyl (NB-C8)

2-(Phenylethynyl)thiophene-5-ethynylphenanthrene (0.26 mmol, 100 mg) and an excess of Co$_2$(CO)$_8$ (0.60 mmol, 205 mg) were used. The crude product was purified by column chromatography using silica gel and hexane (100 %) followed by hexane : CH$_2$Cl$_2$ (75 : 25) as mobile phase which furnished a pure dark green solid. Yield: 143 mg, 0.15 mmol, 57 %

$^1$H NMR (600 MHz, CDCl$_3$): 8.78-8.77 (1H, m), 8.69-8.68 (1H, m), 8.23-8.15 (2H, m), 7.94-7.92 (1H, m), 7.71-7.68 (2H, m), 7.64-7.58 (3H, m), 7.35-7.29 (5H, m), 7.22-7.21 (1H, m) ppm. $^{13}$C NMR (150 MHz, CDCl$_3$): 197.91, 142.90, 142.66, 136.72, 132.21, 131.92, 129.56, 128.72, 128.20, 128.14, 127.95, 127.42, 127.08, 126.14, 125.96, 121.67, 94.95, 80.23 ppm. IR (CH$_2$Cl$_2$): v(CO) 2094, 2088, 2060, 2031, 2014 cm$^{-1}$. 
3.4 Results
3.4.1 UV-vis absorbance studies

Listed in table 1 are the absorbance maxima ($\lambda_{\text{max}}$) and extinction coefficient values ($\varepsilon$) for all compounds in this study. All UV-vis spectra were recorded in spectrophotometric grade CH$_2$Cl$_2$. The absorbance data of diphenylacetylene (PhCCPh) and diphenylacetylene dicobalt hexacarbonyl ($\mu_2$-PhCCPh-Co$_2$(CO)$_6$) have previously been reported (Fig. 17)\textsuperscript{52}

![UV-vis spectra of PhCCPh](image)

Figure 17 UV-vis spectra of PhCCPh (blue line) and PhCCPh-Co$_2$(CO)$_6$ (red line) recorded in CH$_2$Cl$_2$. Spectra have been normalised at their $\lambda_{\text{max}}$.

All compounds (NB-L1 – NB-L8) exhibit strong absorbance bands in the UV-vis region of the spectrum normally associated with ligand localised $\pi$-$\pi^*$ transitions. For the dicobalt hexacarbonyl complexes (NB-C1 – NB-C8) weak low energy transitions are also observed between 580 and 600 nm, extending to 700 nm in some cases. These are assigned to weak CO ($d\pi$) $\rightarrow$ ligand ($\pi$) charge transfer (MLCT) transitions.
<table>
<thead>
<tr>
<th>Ligand</th>
<th>$\lambda_{\text{max}}$ (nm), $\varepsilon$ ($\times 10^4$ M$^{-1}$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PhCCPh</td>
<td>274, 282 (3.08), 290, 300 (2.62), 318</td>
</tr>
<tr>
<td>NB-L1</td>
<td>302 (2.08), 318 (1.61)</td>
</tr>
<tr>
<td>NB-L2</td>
<td>282 (2.11), 288 (1.77), 300 (1.79)</td>
</tr>
<tr>
<td>NB-L3</td>
<td>318 (2.38), 324 (2.02), 338 (1.61)</td>
</tr>
<tr>
<td>NB-L4</td>
<td>300 (1.64), 316 (1.30), 338 (0.18)</td>
</tr>
<tr>
<td>NB-L5</td>
<td>310 (2.81), 326 (2.27), 368 (0.12)</td>
</tr>
<tr>
<td>NB-L6</td>
<td>276 (0.79), 358 (2.19), 370 (2.14)</td>
</tr>
<tr>
<td>NB-L7</td>
<td>276 (1.17), 306 (0.50), 412 (3.72)</td>
</tr>
<tr>
<td>NB-L8</td>
<td>250 (3.32), 310 (1.80), 332 (2.20), 360 (3.12), 374 (2.98), 390 (2.14)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\lambda_{\text{max}}$ (nm), $\varepsilon$ ($\times 10^4$ M$^{-1}$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PhCCPh-Co$_2$(CO)$_6$</td>
<td>280 (1.91), 364 (0.43), 440 (0.20), 560 (0.09)</td>
</tr>
<tr>
<td>NB-C1</td>
<td>282 (1.83), 322 (1.31), 450 (0.15), 568 (0.08)</td>
</tr>
<tr>
<td>NB-C2</td>
<td>282 (4.48), 300 (3.69), 330 (1.26), 444 (0.24), 578 (0.22)</td>
</tr>
<tr>
<td>NB-C3</td>
<td>280 (1.89), 322 (1.43), 464 (0.15), 584 (0.09)</td>
</tr>
<tr>
<td>NB-C4</td>
<td>274 (1.72), 328 (1.24), 458 (0.14), 576 (0.09)</td>
</tr>
<tr>
<td>NB-C5</td>
<td>274 (2.17), 318 (1.67), 458 (0.20), 578 (0.11)</td>
</tr>
<tr>
<td>NB-C6</td>
<td>272 (2.18), 350 (1.76), 464 (0.17), 554 (0.11)</td>
</tr>
<tr>
<td>NB-C7</td>
<td>274 (1.95), 404 (1.68), 440 (1.68), 546 (0.26)</td>
</tr>
<tr>
<td>NB-C8</td>
<td>272 (3.25), 330 (2.21), 366 (1.96), 480 (0.26), 590 (0.21)</td>
</tr>
</tbody>
</table>

*Table 1* UV-vis absorbance data of ligands and corresponding complexes are recorded in CH$_2$Cl$_2$. 
3.4.2 Steady state fluorescence studies

Room temperature emission studies of the compounds and complexes were carried out in CH\textsubscript{2}Cl\textsubscript{2} as were luminescence lifetime measurements using the single photon counting (SPC) technique. Solutions were prepared such that they were isoabsorptive at a selected wavelength having an optical density in solution of approximately 0.2 A.U. Ligands NB-L\textsubscript{1}, NB-L\textsubscript{2}, NB-L\textsubscript{3} and NB-L\textsubscript{4} did not fluoresce and in conjunction with this neither did their metal carbonyl complexes. Ligands NB-L\textsubscript{5}, NB-L\textsubscript{6} and NB-L\textsubscript{7} were found to be weakly emissive, and the corresponding cobalt carbonyl complexes (NB-C\textsubscript{5}, NB-C\textsubscript{6} and NB-C\textsubscript{7}) displayed very weak fluorescence, albeit with lower intensity than that of the ligands. Attachment of the fluorescent phenanthrenyl moiety, as in NB-L\textsubscript{8}, caused an increase in the fluorescence intensity of the molecule. Following coordination of the dicobalt carbonyl moiety, NB-C\textsubscript{8}, a reduction in emission intensity was observed, however there is no significant shift in the position of the emission band, thereby suggesting that the emission is ligand based without major MLCT contribution. The excitation spectra of the emissive compounds had the same profile as the corresponding absorbance spectra further suggesting that the emissive state was ligand based. The emission lifetimes were measured for all emissive compounds and complexes. The emission lifetimes are presented in table 2 below.

<table>
<thead>
<tr>
<th></th>
<th>(\lambda_{em}) (nm)</th>
<th>(\tau) (ns)</th>
<th></th>
<th>(\lambda_{em}) (nm)</th>
<th>(\tau) (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NB-L\textsubscript{5}</td>
<td>386, 404</td>
<td>2.01</td>
<td>NB-C\textsubscript{5}</td>
<td>370</td>
<td>1.98</td>
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<tr>
<td>NB-L\textsubscript{6}</td>
<td>380, 396</td>
<td>2.18</td>
<td>NB-C\textsubscript{6}</td>
<td>404</td>
<td>1.32</td>
</tr>
<tr>
<td>NB-L\textsubscript{7}</td>
<td>467, 646</td>
<td>3.52</td>
<td>NB-C\textsubscript{7}</td>
<td>471</td>
<td>---</td>
</tr>
<tr>
<td>NB-L\textsubscript{8}</td>
<td>403, 425</td>
<td>2.62</td>
<td>NB-C\textsubscript{8}</td>
<td>405, 427</td>
<td>0.54</td>
</tr>
</tbody>
</table>

*Table 2*  
Luminescence lifetimes (298 K) of compounds NB-L\textsubscript{5} – NB-L\textsubscript{8} and the corresponding dicobalt hexacarbonyl complexes NB-C\textsubscript{5} – NB-C\textsubscript{8} recorded in CH\textsubscript{2}Cl\textsubscript{2}.  

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Cyclic voltammetry studies were carried out on the compounds and complexes in a 0.1 M TBAPF$_6$/CH$_3$CN electrolyte solution. Table 3 presents the electrochemical data obtained at room temperature. In all cases one irreversible anodic peak corresponding to the oxidation of the thienyl unit was observed in the range +1.47 to 1.90 V vs. Fc/Fc$^+$ which is in good agreement with the values reported by Hao et al. where the oxidation of the thienyl moiety was observed in the range +1.53 to 1.74 V vs. Ag/Ag$^+$. In some cases oxidation at potentials higher than +1.4 V lead to gradual loss of all characteristic oxidation and reduction potentials and sometimes resulted in deposition of a film onto the working and counter electrode surfaces which is attributed to “polymerisation” of the compound. Electropolymerisation processes are known for thiophene systems and so these compounds require further investigation. Complexation with dicobalt hexacarbonyl caused only minor shifts in the thiophene oxidation potential, with an additional irreversible oxidation and irreversible reduction wave observed for each of the complexes. An irreversible oxidation process was observed in the range +0.88 to 0.99 V vs. Fc/Fc$^+$. This was ascribed to oxidation of the cobalt metal centre and is in agreement with previous studies for cobalt carbonyl systems where oxidation potentials were observed in the range +0.70 to 0.90 V. The irreversible reduction of the cobalt metal centre was observed in the range -0.95 to -1.16 V vs. Fc/Fc$^+$ which corresponds to the reduction of the metal cluster and is in the range reported by Jung et al. Again, in some cases oxidation at potentials higher than +1.4 V lead to loss of all characteristic oxidation and reduction potentials. This phenomenon has been previously observed for dicobalt carbonyl complexes and has been assigned to decomposition of the complex at the electrode surface and perturbs further electrochemical analysis.
<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{pa}$ (V) [Irr]</th>
<th>$E_{pc}$ (V) [Irr]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PhCCPh$^a$</td>
<td>1.92</td>
<td></td>
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<tr>
<td>PhCCPh-Co$_2$(CO)$_6$</td>
<td>0.95, 1.91</td>
<td>-1.06</td>
</tr>
<tr>
<td>NB-L1$^a$</td>
<td>1.65</td>
<td></td>
</tr>
<tr>
<td>NB-C1</td>
<td>0.89, 1.60</td>
<td>-1.03</td>
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<tr>
<td>NB-L2$^a$</td>
<td>1.78</td>
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<tr>
<td>NB-C2</td>
<td>0.88, 1.72</td>
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<tr>
<td>NB-L3$^a$</td>
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<tr>
<td>NB-C3</td>
<td>0.91, 1.41</td>
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<tr>
<td>NB-L4$^a$</td>
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<td>NB-C4</td>
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<tr>
<td>NB-L5$^a$</td>
<td>1.72</td>
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<tr>
<td>NB-C5</td>
<td>0.96, 1.76</td>
<td>-1.16</td>
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<tr>
<td>NB-L6$^a$</td>
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<tr>
<td>NB-C6</td>
<td>0.99, 1.95</td>
<td>-0.89</td>
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<tr>
<td>NB-L7</td>
<td>1.90</td>
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</tr>
<tr>
<td>NB-C7</td>
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<tr>
<td>NB-L8$^a$</td>
<td>1.39, 1.66, 1.99</td>
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<tr>
<td>NB-C8</td>
<td>0.91, 1.39</td>
<td>-0.95</td>
</tr>
</tbody>
</table>

*Table 3* Electrochemical properties measured at room temperature with a scan rate of 0.1 V/s in 0.1 M TBAPF$_6$/CH$_3$CN solution. $E_{pc}$ and $E_{pa}$ correspond to the cathodic and anodic peak potentials respectively, all quoted in volts vs. Fc/Fc$^+$. $^a$ indicates no reduction processes were observed between 0 V and -2.1 V.
Electrochemical analysis of PhCCPh and PhCCPh-Co$_2$(CO)$_6$ was carried out as a standard to delineate the effect of the thienyl moiety. The cyclic voltammograms of ligands and complexes are included in appendices B1 – B7.

The cyclic voltammogram of PhCCPh is displayed in figure 18 (a). The CV of the reference compound shows a single irreversible oxidation process associated with the generation of the cation radical, with no second oxidation process out to the solvent limit. No reduction processes were observed. The $E_{pa}$ value of the oxidation wave was +1.92 V vs. Fc/Fc$^+$ and was due to oxidation of the phenyl moiety. The cyclic voltammogram of PhCCPh-Co$_2$(CO)$_6$ (Fig. 18, b) displays the oxidation due to the phenyl moiety at +1.91 V vs. Fc/Fc$^+$ and an additional irreversible oxidation was observed at +0.95 V vs. Fc/Fc$^+$ which was assigned to oxidation of the cobalt metal centre and is in agreement with previous literature observations.$^{55}$ An irreversible reduction wave was observed at $E_{pc}$ = -1.06 V vs. Fc/Fc$^+$. The reduction peak was attributed to a monoelectronic reduction process at the metal centre. Upon scan reversal in CV, no coupled anodic peak was observed, however a new irreversible peak at +0.22 V appeared. This behaviour resembles other reported ($\mu_2$-alkyne)Co$_2$(CO)$_6$ derivatives and indicates that a reduction process followed by fast decomposition of the radical anion into a variety of fragments occurred.$^{57}$ At higher potentials a coating formed on both the working and counter electrode. The reduction peak a -0.79 V vs. Fc/Fc$^+$ is assigned to the reduction of this chemically adsorbed cobalt containing product.$^{60}$
Figure 18 Cyclic voltammogram of PhCCPh (a) and PhCCPh-Co$_2$(CO)$_6$ (b) showing oxidation and reduction waves.
The cyclic voltammogram of NB-L1 is displayed in figure 19 (a). An irreversible anodic wave was observed at +1.65 V vs. Fc/Fc\(^+\). By analogy to the previous system this process corresponds to the initial generation of the cation radical species. It was ascribed to the oxidation of the thienyl unit by comparison with the oxidation peak potential of thiophene (E\(p\) = 1.73 V).\(^{58}\) No second oxidation process was observed out to the solvent limit, by which stage deposition onto the electrodes occurred indicating that degradation (overoxidation) had occurred. No reduction processes were observed. The corresponding complex NB-C1 displayed two irreversible oxidation peaks (Fig. 19, b). The oxidation of the cobalt metal centre occurred at +0.89 V vs. Fc/Fc\(^+\) while oxidation of the thienyl moiety occurred at +1.60 V vs. Fc/Fc\(^+\). The irreversible reduction of the metal centre was observed at -1.03 V vs. Fc/Fc\(^+\). On following sweeps new oxidations at +0.14 V and +0.26 V were observed as well as a reduction at -0.74 V. These are attributed to the redox chemistry of a variety of cobalt degradation products discussed above.\(^{57}\)
Figure 19  Cyclic voltammogram of NB-L1 (a) and NB-C1 (b) showing oxidation and reduction waves.
3.4.4 Steady state photolysis

Broadband photolysis ($\lambda_{\text{exc}} > 520$ nm, $\lambda_{\text{exc}} > 410$ nm and $\lambda_{\text{exc}} > 320$ nm) of the dicobalt hexacarbonyl complexes in the presence of the trapping ligand, PPh$_3$, resulted in the formation of a pentacarbonyl species. In each case, product bands were assigned by comparison with carbonyl bands of Co$_2$(CO)$_5$ type species in the literature.$^{27,40,41}$ In general, irradiation at $\lambda > 520$ nm resulted in the weak production of the triphenylphosphine trapped pentacarbonyl species. Following irradiation at $\lambda > 410$ nm an improved efficiency for production of the pentacarbonyl formation was observed, while irradiation at $\lambda > 320$ nm results in greatly improved efficiency for pentacarbonyl formation. Furthermore, formation of the tetracarbonyl photoproduct was observed under high energy irradiation ($\lambda > 320$ nm). The IR bands observed and assigned to formation of the trapped photoproducts (Co$_2$(CO)$_5$ species and Co$_2$(CO)$_4$ species) were in good agreement with those previously observed by Chia,$^{28}$ Gordon$^{40}$ and Long.$^{41}$ Table 4 gives the IR data for the parent dicobalt hexacarbonyl complexes and the photoproducts observed. Three steady state photolysis spectra are included and discussed in more detail. The remainder are included in appendices C1 – C5.
<table>
<thead>
<tr>
<th>Complex</th>
<th>$\nu$(CO) (cm$^{-1} \pm 2$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NB-C1-Co$_2$(CO)$_6$(parent)</td>
<td>2091, 2058, 2030</td>
</tr>
<tr>
<td>NB-C1-Co$_2$(CO)$_5$(PPh$_3$)</td>
<td>2064, 2018, 2005</td>
</tr>
<tr>
<td>NB-C1-Co$_2$(CO)$_4$(PPh$_3$)$_2$</td>
<td>1996, 1972, 1960</td>
</tr>
<tr>
<td>NB-C2-Co$_2$(CO)$_6$(parent)</td>
<td>2090, 2055, 2028</td>
</tr>
<tr>
<td>NB-C2-Co$_2$(CO)$_5$(PPh$_3$)</td>
<td>2064, 2018, 2005</td>
</tr>
<tr>
<td>NB-C3-Co$_2$(CO)$_6$(parent)</td>
<td>2091, 2058, 2031</td>
</tr>
<tr>
<td>NB-C3-Co$_2$(CO)$_5$(PPh$_3$)</td>
<td>2065, 2020, 2007</td>
</tr>
<tr>
<td>NB-C3-Co$_2$(CO)$_4$(PPh$_3$)$_2$</td>
<td>1984, 1973, 1951, 1941</td>
</tr>
<tr>
<td>NB-C4-Co$_2$(CO)$_6$(parent)</td>
<td>2091, 2059, 2032</td>
</tr>
<tr>
<td>NB-C4-Co$_2$(CO)$_5$(PPh$_3$)</td>
<td>2065, 2019, 2007</td>
</tr>
<tr>
<td>NB-C4-Co$_2$(CO)$_4$(PPh$_3$)$_2$</td>
<td>1997, 1972, 1943</td>
</tr>
<tr>
<td>NB-C5-Co$_2$(CO)$_6$(parent)</td>
<td>2092, 2057, 2030</td>
</tr>
<tr>
<td>NB-C5-Co$_2$(CO)$_5$(PPh$_3$)</td>
<td>2065, 2019, 2007</td>
</tr>
<tr>
<td>NB-C5-Co$_2$(CO)$_4$(PPh$_3$)$_2$</td>
<td>1997, 1972, 1943</td>
</tr>
<tr>
<td>NB-C6-Co$_2$(CO)$_6$(parent)</td>
<td>2095, 2062, 2035</td>
</tr>
<tr>
<td>NB-C6-Co$_2$(CO)$_5$(PPh$_3$)</td>
<td>2068, 2024, 2011</td>
</tr>
<tr>
<td>NB-C6-Co$_2$(CO)$_4$(PPh$_3$)$_2$</td>
<td>1985, 1977, 1955, 1944</td>
</tr>
<tr>
<td>NB-C7-Co$_2$(CO)$_6$(parent)</td>
<td>2094, 2061, 2034</td>
</tr>
<tr>
<td>NB-C7-Co$_2$(CO)$_5$(PPh$_3$)</td>
<td>2067, 2021, 2009</td>
</tr>
<tr>
<td>NB-C7-Co$_2$(CO)$_4$(PPh$_3$)$_2$</td>
<td>1974, 1960</td>
</tr>
<tr>
<td>NB-C8-Co$_2$(CO)$_6$(parent)</td>
<td>2094, 2088, 2060, 2031</td>
</tr>
<tr>
<td>NB-C8-Co$_2$(CO)$_5$(PPh$_3$)</td>
<td>2065, 2053, 2021, 2005, 1975</td>
</tr>
</tbody>
</table>

Table 4: IR data for dicobalt hexacarbonyl complexes and the corresponding photoproducts produced following broadband irradiation in hexane solution in the presence of PPh$_3$. 
Extended broadband photolysis of the dicobalt hexacarbonyl complex, NB-C1, at $\lambda_{\text{exc}} > 520$ nm for 30 minutes resulted in minor bleaching of the parent absorbance bands at 2091, 2058 and 2030 cm$^{-1}$ and generation of weak product bands at 2064, 2018 and 2005 cm$^{-1}$ (Fig. 20). Subsequent photolysis at $\lambda_{\text{exc}} > 410$ nm for 12 minutes resulted in an increase in the intensity of these bands, assigned to formation of the pentacarbonyl species, NB-C1-Co$_2$(CO)$_5$(PPh$_3$)$_2$. Concomitant generation of weak bands at 1996, 1972 and 1960 cm$^{-1}$ was observed which were tentatively assigned to generation of the tetracarbonyl species, NB-C1-Co$_2$(CO)$_4$(PPh$_3$)$_2$. Continued irradiation at $\lambda_{\text{exc}} > 320$ nm for 5 minutes caused further depletion of parent bands and a notable intensification of the photoproduct bands. The assignment of bands to the pentacarbonyl species NB-C1-Co$_2$(CO)$_5$(PPh$_3$)$_2$ and tetracarbonyl species NB-C1-Co$_2$(CO)$_4$(PPh$_3$)$_2$, were based on similarities with those observed by Coleman et al.$^{27}$ and Arnanz et al.$^{60}$ following formation of trapped pentacarbonyl and tetracarbonyl species respectively.

![Figure 20](image)

**Figure 20**  *Infrared difference spectra following irradiation of NB-C1 in hexane with PPh$_3$ at $\lambda_{\text{exc}} > 520$ nm (black lines, 30 minutes total irradiation), $\lambda_{\text{exc}} > 410$ nm (red lines, 12 minutes total irradiation) and $\lambda_{\text{exc}} > 320$ nm (blue lines, 5 minutes total irradiation). Negative bands indicate bleaching of the parent complex while positive bands indicate generation of the pentacarbonyl and tetracarbonyl species.*
The aldehyde complex, **NB-C6**, was subjected to broadband irradiation ($\lambda_{\text{exc}} > 520$ nm for 30 minutes, $\lambda_{\text{exc}} > 410$ nm for 10 minutes and $\lambda_{\text{exc}} > 320$ nm for 3 minutes) (Fig. 21). Minor depletion of the parent hexacarbonyl bands at 2095, 2062 and 2035 cm$^{-1}$ was observed upon $\lambda_{\text{exc}} > 520$ nm irradiation with the growth of positive bands assigned to the pentacarbonyl complex **NB-C6-Co$_2$(CO)$_5$(PPh$_3$)$_2$** at 2068, 2024 and 2011 cm$^{-1}$. Irradiation with $\lambda_{\text{exc}} > 410$ nm resulted in intensification of the pentacarbonyl product bands (2068, 2024, 2011 cm$^{-1}$) and generation of bands at 1985, 1977, 1955 and 1944 cm$^{-1}$ which were attributed to the tetracarbonyl product, **NB-C6-Co$_2$(CO)$_4$(PPh$_3$)$_2$**. Photolysis of the pentacarbonyl species, **NB-C6-Co$_2$(CO)$_5$(PPh$_3$)$_2$**, also occurred, as the bands at 2068, 2024 and 2011 cm$^{-1}$ decreased in intensity. The bands at 1985, 1977, 1955 and 1944 cm$^{-1}$ increased in absorbance indicating increased production of the tetracarbonyl product **NB-C6-Co$_2$(CO)$_4$(PPh$_3$)$_2$**.

**Figure 21** Infrared difference spectra following irradiation of **NB-C6** in hexane with PPh$_3$ at $\lambda_{\text{exc}} > 520$ nm (black lines, 30 minutes total irradiation), $\lambda_{\text{exc}} > 410$ nm (red lines, 10 minutes total irradiation) and $\lambda_{\text{exc}} > 320$ nm (blue lines, 3 minutes total irradiation). Negative bands indicate bleaching of the parent complex while positive bands indicate generation of the pentacarbonyl and tetracarbonyl species.
Extended broadband photolysis of **NB-C8** at $\lambda_{\text{exc}} > 520$ nm for 30 minutes resulted in bleaching of the parent bands at 2094, 2088, 2060 and 2031 cm$^{-1}$ and the generation of weak product bands at 2065, 2053, 2021, 2009 and 1974 cm$^{-1}$ due to pentacarbonyl formation (Fig. 22). These IR bands continued to grow following irradiation at $\lambda_{\text{exc}} > 410$ nm for a further 10 minutes. Photolysis $\lambda_{\text{exc}} > 320$ nm for 3 minutes resulted in the depletion of the photoproduct bands at 2065 and 2053 cm$^{-1}$. This indicated depletion of the pentacarbonyl photoproduct and the generation of the tetracarbonyl species. The bands at 2021 cm$^{-1}$ splits into two bands, 2023 and 2019 cm$^{-1}$ and continued to increase in intensity. The band at 2009 cm$^{-1}$ shifted to lower wavenumber 2004 cm$^{-1}$ and increased in intensity. Bands indicative of tetracarbonyl formation (2023, 1995, 1983, 1975 and 1948 cm$^{-1}$) also increased in intensity following irradiation at $\lambda_{\text{exc}} > 320$ nm (5 minutes). The larger number of bands, both for the parent hexacarbonyl complex **NB-C8** and photochemically generated pentacarbonyl and tetracarbonyl complexes was attributed to the two dicobalt hexacarbonyl centres in this molecule. The new absorbance bands are ascribed to the formation of the trapped species at both of the metal centres.

**Figure 22** Infrared difference spectra following irradiation of **NBC8** in hexane with $PPh_3$ at $\lambda_{\text{exc}} > 520$ nm (black, 30 minutes total irradiation), $\lambda_{\text{exc}} > 410$ nm (red, 10 minutes total irradiation) and $\lambda_{\text{exc}} > 320$ nm (blue, 3 minutes total irradiation). Negative bands indicate bleaching of the parent complex while positive bands indicate generation of the photoproduct.
3.4.5 Quantum yield of CO loss

The quantum yield of the photoinduced expulsion of CO from three ($\mu_2$-alkyne)Co$_2$(CO)$_6$ complexes was measured in a cyclohexane solution at 298 K. The experiments were undertaken for PhCCPh-Co$_2$(CO)$_6$, ThCCPh-Co$_2$(CO)$_6$ (NB-C1) and FeCCH-Co$_2$(CO)$_6$ (Fig. 23). FeCCH-Co$_2$(CO)$_6$ was synthesised according to literature methods and is detailed in appendix D. Potassium ferrioxalate actinometry was used to measure the incident light intensity. A 200 W Hg-Xe arc lamp was used and the required Hg spectral line selected using interface filters. Measurements were made using four excitation wavelengths of 313, 365, 405 and 546 nm. Triphenylphosphine was used as a trapping ligand for the photoproduced ($\mu_2$-alkyne)Co$_2$(CO)$_5$ species. Prior to the photolysis experiments, the trapped ($\mu_2$-alkyne)dicobalt pentacarbonyl species was isolated and characterised (appendices E1-E3). In all cases a new absorbance centred at approximately 400 nm was observed for the triphenylphosphine trapped pentacarbonyl species (Fig. 24), and it was at 400 nm that quantum yields were calculated.

![Figure 23](image)

*Figure 23* Reaction following photolysis of the dicobalt hexacarbonyl complexes and the trapped pentacarbonyl species produced.
Figure 24 Absorbance spectra of dicobalt hexacarbonyl complexes (blue lines), $\text{PhCCPh-Co}_2(\text{CO})_6$ (a), $\text{ThCCPh-Co}_2(\text{CO})_6$ (b), $\text{FcCCH-Co}_2(\text{CO})_6$ (c) and corresponding trapped pentacarbonyl complex (red lines) recorded in cyclohexane. Spectra have been normalised at their $\lambda_{\text{max}}$. 
Photosubstitution of the three complexes was monitored by UV-vis spectroscopy. In each experiment the number of photolysed molecules was determined by comparison of UV-vis spectra taken before and after photolysis. Further experimental details and all calculations are given in appendix F. Conversions were driven to a maximum of 10% to minimise the effect of product absorbance at the excitation wavelength.

The quantum yield for CO loss under steady state irradiation (Table 5) was determined by application of the Beer-Lambert law. The results show that the efficiency of CO loss is both wavelength and complex dependant.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Irradiation Wavelength</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>313 nm</td>
</tr>
<tr>
<td><strong>PhCCPh-Co₂(CO)₆</strong></td>
<td>0.078</td>
</tr>
<tr>
<td><strong>ThCCPh-Co₂(CO)₆</strong></td>
<td>0.145</td>
</tr>
<tr>
<td><strong>FcCCH-Co₂(CO)₆</strong></td>
<td>0.269</td>
</tr>
</tbody>
</table>

*Table 5* Quantum yields for CO loss recorded in cyclohexane.
3.4.6 Picosecond time resolved infrared studies

A picosecond time resolved infrared study of the photochemical activation of (μ₂-alkyne)Co₂(CO)₆ complexes was carried out for PhCCPh-Co₂(CO)₆, ThCCPh-Co₂(CO)₆ and FeCCH-Co₂(CO)₆ in solution at room temperature (298 K). Photo-excitation (λ_{exc} = 400 nm, τ_{FWHM} = 150 fs) of the three complexes (and in the case of FeCCH-Co₂(CO)₆ also at 532 nm) resulted in depletion of the ground state ν(CO) bands of all three complexes with the appearance of new bands in the ν(CO) region. All complexes exhibited similar spectral changes and the kinetics were largely solvent independent. The photoproduct IR bands undergo vibrational cooling (over ~10 ps) with a shift in wavenumber to higher frequency. These new bands decay with complete product recovery of the initial spectrum on a picosecond timescale.

Lifetimes of the excited state transient species observed in the TRIR experiments were calculated and are presented in table 6 below. The kinetics of the recovery was largely solvent independent.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Lifetime (ps)</th>
<th>THF</th>
<th>CH₃CN</th>
<th>Pentane</th>
</tr>
</thead>
<tbody>
<tr>
<td>PhCCPh-Co₂(CO)₆</td>
<td>70</td>
<td>69</td>
<td></td>
<td>71</td>
</tr>
<tr>
<td>ThCCPh-Co₂(CO)₆</td>
<td>63</td>
<td></td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>FeCCH-Co₂(CO)₆</td>
<td>38</td>
<td>50</td>
<td></td>
<td>−</td>
</tr>
</tbody>
</table>

Table 6 Lifetimes for the excited state transient species produced following excitation at 400 nm. Lifetimes are +/- 5 ps.
3.4.6.1 TRIR studies of PhCCPh-Co$_2$(CO)$_6$

![Transient absorbance difference spectra](image)

Figure 25 Transient absorbance difference spectra at 10, 20, 50, 100 and 250 ps, following excitation of PhCCPh-Co$_2$(CO)$_6$ in THF at 400 nm.

Photolysis of PhCCPh-Co$_2$(CO)$_6$ ($\lambda_{\text{exc}} = 400$ nm, $\tau_{\text{FWHM}} = 150$ fs) in THF solution at room temperature resulted in depletion of the ground state $\nu$(CO) peaks at 2089, 2055 and 2028 cm$^{-1}$ within 1 ps (first spectrum after 1 ps delay) (Fig. 25). Three new peaks were formed at 2070, 2040 and 2009 cm$^{-1}$. The IR bands underwent vibrational cooling (over ~10 ps), with a shift in wavenumber to higher frequency, to 2073, 2042 and 2012 cm$^{-1}$. The bands relax to the ground state with a lifetime of 70 ps with concomitant recovery of the parent bleaches.

In acetonitrile the three parent bands (2089, 2055 and 2031 cm$^{-1}$) are depleted within the laser pulse with concomitant formation of three new bands at 2074, 2041 and 2006 cm$^{-1}$ following irradiation ($\lambda_{\text{exc}} = 400$ nm). These new bands undergo vibrational cooling and shift to 2082, 2048 and 2019 cm$^{-1}$ where decay of the excited state is fully complete with a lifetime of 69 ps. No residual bleaches were observed in the final spectrum (appendix G1).
In pentane, irradiation at 400 nm depleted the parent peaks (2089, 2055 and 2031 cm$^{-1}$) and produced new peaks at 2069, 2041, 2016 and 2006 (sh) cm$^{-1}$ within the instrument response time of 1 ps (appendix G2). The peaks then shift to 2079, 2045 and 2021 cm$^{-1}$ over 10 ps due to vibrational cooling. Over the next 250 ps, the product peaks decay back to the ground state with a lifetime of 71 ps and simultaneous recovery of the parent bleaches was observed.
3.4.6.2 TRIR studies of ThCCPh-Co$_2$(CO)$_6$

![Figure 26](image)

Figure 26 Transient absorbance difference spectra at 10, 25, 50, 100 and 250 ps, following excitation of ThCCPh-Co$_2$(CO)$_6$ in CH$_3$CN at 400 nm.

Comparable spectroscopic changes in the ν(CO) region were observed for ThCCPh-Co$_2$(CO)$_6$. In CH$_3$CN solution, photolysis of the hexacarbonyl complex caused depletion of the infrared bands at 2091, 2058 and 2030 cm$^{-1}$ (negative signals in Fig. 26) within the excitation pulse, with formation of bands initially at 2076, 2048 and 2006 cm$^{-1}$. The product (positive) peaks undergo vibrational cooling on the picosecond timescale and shift to 2081, 2048 and 2016 cm$^{-1}$. The transient bands relax to the ground state with a lifetime of 63 ps. Importantly, compete recovery of the parent bands was also observed.
3.4.6.3 TRIR studies of FcCCH-Co$_2$(CO)$_6$

Figure 27 Transient absorbance difference spectra at 10, 20, 50, 75 and 250 ps, following excitation of FcCCH-Co$_2$(CO)$_6$ in THF at 532 nm.

Akin to the previous results, irradiation of FcCCH-Co$_2$(CO)$_6$ in acetonitrile solution at $\lambda_{\text{exc}}$ = 400 nm caused changes in the $\nu$(CO) bands in the infrared spectrum (appendix G3). The parent bands of FcCCH-Co$_2$(CO)$_6$ observed at 2090, 2052 and 2028 cm$^{-1}$ depleted and three new bands at 2071, 2042 and 2005 cm$^{-1}$ appeared within the laser pulse. The IR bands undergo vibrational cooling (over ~10 ps), with a shift in wavenumber to higher frequency, to 2080, 2046 and 2009 cm$^{-1}$. The bands decay a lifetime of 50 ps with concomitant recovery of the parent bleaches.

Photolysis was carried out at 532 nm to ascertain if there was a wavelength dependence on the photochemical processes observed in the complexes. Irradiation of a solution of FcCCH-Co$_2$(CO)$_6$ in THF resulted in a bleaching of the parent IR bands with simultaneous formation of new bands at 2073, 2041, 2008 and 1997 (sh) cm$^{-1}$ (Fig. 27). These bands undergo vibrational cooling and shift to 2079, 2041, 2007 and 1997 (sh) cm$^{-1}$ where they fully decay and the parent bands recover to pre-irradiation levels as observed previously when using 400 nm excitation.
Photoexcitation of carbonyl complexes often results in photosubstitution of a carbonyl group by the solvent and formation of a solvent trapped pentacarbonyl species ($\mu_2$-alkyne)Co$_2$(CO)$_5$(solvent). To rule out the possibility of a solvent pentacarbonyl species which absorbs in a similar region to either the parent complex, or underneath the new bands observed in this study, a trapping ligand was employed. A solution of FeCCH-Co$_2$(CO)$_6$ in THF was doped with an excess of triphenylphosphine and irradiated at $\lambda_{\text{exc.}} = 532$ nm. Spectroscopic changes in the $\nu$(CO) region correspond well with those previously observed (appendix G4). The parent bands are depleted and new bands are observed at 2073, 2041, 2008 and 1997 cm$^{-1}$ within 1 ps. The new bands undergo vibrational cooling and shift to 2084, 2046 and 2007 cm$^{-1}$. No new infrared bands were observed on the nanosecond timescale that could be assigned to ($\mu_2$-alkyne)Co$_2$(CO)$_5$(PPh$_3$) indicating that photosubstitution did not occur for this system within these experimental conditions. This is in contrast to steady state photolysis where, in the presence of PPh$_3$, the mono- and subsequently di-substituted complexes formed (appendix H).
3.5 Discussion
3.5.1 Synthesis and spectroscopic characterisation

Ligands NB-L1 – NB-L5 have been previously synthesised and spectroscopic data were in agreement with reported data. All other ligands and all complexes are novel compounds. The NMR spectroscopic data ($^1$H and $^{13}$C) for ligands and complexes were consistent with their formulation. In the $^1$H NMR spectra signals due to the thiophene ring(s) in addition to complex multiplets due to aromatic protons were observed in the range 7.0 – 8.5 ppm. In $^{13}$C NMR spectra, the signals belonging to the thiophene ring (C₂, C₃, C₄ and C₅, Fig. 28) and the alkynyl units (C₆ and C₇, Fig. 28) were observed in the aromatic region of the spectrum. The signals of the free and coordinated acetylene units were easily observed in the region 74-100 ppm. The metal carbonyl resonances in all the complexes appeared as one signal at ~199 ppm.

![Figure 28](thienyl_and_ethynyl_carbons.png)  
Figure 28 Numbering of thienyl and ethynyl carbons.

The IR spectra in the carbonyl region for the complexes show signals corresponding to terminal carbonyl ligands only. These spectral patterns are similar to those observed for previously reported alkyne dicobalt carbonyl complexes.²⁷, ⁴¹ The absence of the alkyne stretch, $\nu$(C≡C), in the region of 2200 cm⁻¹ indicated that the alkyne bond has lost its triple bond character and was coordinated to Co₂(CO)₆.
3.5.2 UV-vis absorbance studies

All compounds in this chapter exhibit strong absorbance bands in the UV-vis region of the spectrum normally associated with ligand localised $\pi \rightarrow \pi^*$ transitions. The absorbance spectra of some of the ligands and complexes are shown and discussed below.

The $C_3 – C_4$ bond in the thiophene ring was reported to have less double bond character than the $C_2 – C_3$ bond$^{59}$ and as a consequence the overall conjugation of the 3-ethynylthiophene derivatives, NB-L2 and NB-L4, is expected to be lower than in the 2-ethynylthiophene derivatives, NB-L1 and NB-L3. This argument is supported by the electronic absorbance spectra for the compounds (Fig. 29). The $\lambda_{\text{max}}$ for NB-L1 and NB-L3 are observed at 302 and 318 nm however the $\lambda_{\text{max}}$ for NB-L2 and NB-L4 are significantly blue shifted to 282 and 300 nm respectively. This hypsochromic shift of 20 nm (for NB-L1 $\rightarrow$ NB-L2) and 18 nm (for NB-L3 $\rightarrow$ NB-L4) in the absorbance $\lambda_{\text{max}}$ indicated less overall conjugation within the molecule. A similar shift was previously observed by Arnanz et al.$^{60}$ Sakar and Hanley also observed a hypsochromic shift in absorbance spectra when thiophenes were conjugated through the $C_3$ or $C_4$ position in [18]annulene ring systems.$^{61}$

![Figure 29](image-url)  
*Figure 29* Overlay of the electronic absorbance spectra of NB-L1, NB-L2, NB-L3 and NB-L4 in CH$_2$Cl$_2$. Spectra normalised at their $\lambda_{\text{max}}$. 

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The absorbance spectra of ligands NB-L1, NB-L5, NB-L6 and NB-L7 are presented in figure 30. The absorbance $\lambda_{\text{max}}$ are bathochromically shifted with appropriate substitution. On replacing the H at the thien-5-yl position in NB-L1 with the more electronegative bromine (NB-L5), aldehyde (NB-L6) and dicyanovinyl unit (NB-L7) the absorbance maxima shifts from 318 nm to 326 nm to 358 nm to 412 nm respectively. This is possibly due to an increase in electron delocalisation within the molecule on adding more electron accepting terminal groups. This is in agreement with the results published by Coleman et al. where terminal group substitution affected the absorbance of organic molecules.\textsuperscript{27}

![Figure 30](image.png)

Figure 30  Overlay of the UV-vis absorbance spectra of NB-L1, NB-L5, NB-L6 and NB-L7 in CH$_2$Cl$_2$. Spectra normalised at their $\lambda_{\text{max}}$.

Coordination of the dicobalt carbonyl moiety (NB-C1 – NB-C8) resulted in broader absorbance bands with less definition in the electronic spectrum. Figure 31 depicts the change in absorbance upon coordination of the metal carbonyl to the ethynyl moiety for ligand and complex pairs, NB-L3/NB-C3 and NB-L5/NB-C5. The high energy transitions are now $\pi-\pi^*$ with metal - $\pi^*$ ($M =$ Co) transitions. Ligand field transitions maybe present but the contribution will be small in relation to $\pi-\pi^*$ transitions. For all the Co$_2$(CO)$_6$ complexes, weak low energy bands are observed between 430 and 600 nm which extend to approximately 680 nm. These may be assigned to weak Co (d$\pi$) $\rightarrow$ ligand ($\pi$) charge transfer (MLCT) transitions and weak d-d transitions between the two metal centres. The
metal upsets the symmetry in the system and that changes how the high energy $\pi-\pi^*$ transition absorbs. The fine structure of the transitions still exists but they are not resolved as in the free ligand.

Figure 31  Absorbance spectra of ligand and complex pairs $\text{NB-L3}/\text{NB-C3}$ (a) and $\text{NB-L5}/\text{NB-C5}$ (b) recorded in $\text{CH}_2\text{Cl}_2$. Spectra normalised at their $\lambda_{\text{max}}$. 
3.5.3 Steady state fluorescence studies

Diphenylacetylene has previously been reported to have a weak emission at room temperature in CH$_2$Cl$_2$ however at low temperature (77 K) an intense well resolved emission was recorded.$^{52b}$ This temperature dependence of emission is attributed to the close vicinity of the S$_2$ and S$_1$ excited states. The latter is a non-emissive “dark” state with a distorted geometry. The activation energy barrier renders the S$_2 \rightarrow$ S$_1$ decay thermally activated and operative at room temperature the result of which is the fast depopulation of S$_2$ causing a very weak and short lived emission. The ground state of diphenylacetylene belongs to the D$_{2h}$ point group. Hirata et al. carried out picosecond time resolved absorbance measurements and reported a “bright” state with a fluorescent lifetime of about 8 ps which is a precursor to the dark state.$^{62}$ The fluorescing state was assigned to the higher singlet state.

The excited-state dynamics of most organic molecules is concerned with low-lying excited states of π-π* character. More recently computational and experimental studies on aromatic ethynes show that the bound excited state of a π-σ* configuration which rises from the promotion of an electron from the aromatic π orbital to the σ* orbital, localised on the −C≡CH, can be low-lying and has pronounced effects on the fluorescence of these molecules.$^{63}$ TD-DFT was used to probe these low-lying excited states. The results indicated that the lowest-energy singlet state is the π-π* state in linear compounds of D$_{2h}$ symmetry, the non-emissive π-σ* state is the lowest energy in bent C$_{2h}$ symmetry compounds. The quantum chemical calculations indicate that due to the differing geometry of the π-σ* state relative to that of the fluorescent π-π* state, the π-σ* state crosses the fluorescent π-π* state along the nuclear coordinate involving bending of the −C≡CH triple bonds. The crossing between the bright π-π* state and the dark (or very weakly fluorescent) π-σ* state can account for loss of fluorescence at higher temperatures in solution. A threshold temperature for the thermal quenching of fluorescence was found to be ~120 K for diphenylacetylene. However the attachment of an electron withdrawing group (such as –CN) to diphenylacetylene increases the energy of the π-σ* state and moves the π-π*/π-σ* intersection far away from the Franck-Condon region of the initially prepared π-π* state. The π-π* $\rightarrow$ π-σ* state switch is therefore not expected to occur in diphenylacetylene with an electron-withdrawing substituent. Extension of the
computational study to di-2-thienylacetylene indicated that the dark $\pi$-$\sigma^*$ state is very slightly above the lowest energy $^1\pi$-$\pi^*$ state at the linear geometry. The state crossing from the $^1\pi$-$\pi^*$ to the $^1\pi$-$\sigma^*$ state is predicted to involve little (if any) energy barriers. Consistent with this prediction, di-2-thienylacetylene does not exhibit fluorescence in solution at room temperature.

Diphenylacetylene was measured as a model compound. It displayed a weak emission with $\lambda_{\text{max}} = 325$ nm. The linear organic conjugated molecules (NB-L1 – NB-L7) display very low emission or no emission at all. This is not surprising. Nb-L1, Nb-L2, Nb-L3 and Nb-L4 did not fluoresce. Nb-L1 was previously reported to be non-fluorescent.63 The other ligands, Nb-L2, Nb-L3 and Nb-L4, also possess $C_{2h}$ symmetry and as such were not expected to fluoresce. According to Zgierski, crossing the state from the $^1\pi$-$\pi^*$ to the $^1\pi$-$\sigma^*$ is facile and results in a quenching of fluorescence.63

The authors also noted that attachment of an electron withdrawing group to diphenylacetylene caused the compound to become weakly fluorescent.63 For compounds Nb-L5, Nb-L6 and Nb-L7 with electron withdrawing groups at the thien-5-yl position weak fluorescence was observed. A substantial red shift was noted in the emission maxima of Nb-L7 (Table 2). This was attributed to improved electron accepting ability of the dicyanovinyl unit. Following coordination with Co$_2$(CO)$_6$ a reduction in emission intensity was observed, although no change in the position of the emission band was observed. This suggested that in complexes Nb-C5 - Nb-C7, the observed emission bands were ligand based without much contribution from the metal centre.

By incorporating a luminescent organic chromophore into linear organic molecules the emission of such species can be greatly increased. This was the case for the ligand and complex pair Nb-L8/Nb-C8. They were more luminescent at room temperature (298 K) and showed the highest emission intensity within the study (Fig. 32). Upon complexation the emission bands were significantly reduced in intensity. However no shift in band position or generation of new emission bands was observed. This suggested that for both Nb-L8 and Nb-C8 the emission is solely ligand based.
Figure 32  Room temperature emission spectra of compounds NB-L8 (blue line) and NB-C8 (red line) recorded in CH$_2$Cl$_2$ solution following excitation at 332 nm. Solutions were isoabsorptive 0.2 AU at $\lambda_{exc} = 332$ nm.

An increase in fluorescence lifetime was observed with increasing the electronegativity of the terminal substituent on the organic ligand (1.94, 2.18 and 3.52 ns for NB-L5, NB-L6 and NB-L7 respectively). One possibility for the increase in lifetimes along this series is the increase in electron delocalisation within the molecule on replacing the terminal moiety at the thien-5-yl position. The emission intensity and lifetimes of the dicobalt complexes were less than those of the uncomplexed ligands. This was to be expected and has been observed previously. It is attributed to the heavy atom effect. The lifetime of NB-L8 was measured as 2.62 ns while that of the carbonyl complex NB-C8 was found to decrease to 0.56 ns at room temperature. Low temperature (77 K) emission studies showed no change in the emission band of NB-C8 however a lifetime of 2.19 ns was obtained.
3.5.4 Electrochemistry

Again comparing ligands NB-L1 with NB-L2 and NB-L3 with NB-L4 showed how the effective conjugation in the ligands affected the electrochemical properties. Ligands NB-L2 and NB-L4 which possess lesser overall conjugation were oxidised at higher potentials than NB-L1 and NB-L3. It is noteworthy that NB-L2 and NB-L4 show greater overall chemical stability than the closely related species NB-L1 and NB-L3 derived from 2-thiophene. Arnanz et al. observed similar redox properties which the authors attributed to steric arguments.60

Compounds NB-L1, NB-L5 and NB-L7 are sequentially oxidised at higher potentials. This is due to the inductive effects of the bromine and dicyanovinyl units attached to the thien-5-yl position. The bromine atom in NB-L5 caused a 70 mV shift to higher potential while the dicyanovinyl moiety caused a shift of 250 mV. This effect of electron withdrawing substituents on the oxidation potentials was previously observed by Zhao and co workers.64 Thus the addition of an electron withdrawing terminal groups, increased electron delocalisation within the molecule and as a result stabilised the molecules. A similar effect was observed for the corresponding dicobalt hexacarbonyl complexes. Replacement of the H with an electron withdrawing group as in complex NB-C5 had a similar influence on the oxidation potentials of the complex compared to NB-C1. A positive shift of 160 mV in the cathodic direction was observed for the thienyl oxidation when comparing the two complexes.

In all complexes the observed redox behaviour was typical of dicobalt hexacarbonyl complexes. The Co₂(CO)₆ entity bound to the alkyne undergoes an irreversible oxidation and an irreversible reduction followed by the fast decomposition of the radical anion into a variety of fragments (EC mechanism).65

The electrogenerated monoanion is very unstable and undergoes fast cleavage of the Co-Co bond which produced Co(CO)₄⁺. This species was observed in the subsequent oxidation sweep where the Co(CO)₄⁺ fragment was oxidised to the radical Co(CO)₄⁺. A subsequent reduction is ascribed to the reduction of degradation products that were chemically adsorbed onto the electrode. This behaviour was reported previously in related hexacarbonyl complexes of the form (μ₂-alkyne)Co₂(CO)₆.66 The reduction corresponds to
the formation of the radical anion in which the extra electron occupies a predominantly metal-metal antibonding orbital.\textsuperscript{67} Subsequently, rapid metal-metal bond cleavage takes place and disintegration of the anion radical, into variety of fragments, occurs.

The stabilising effect observed for the ligands did not bestow stability onto the complexes. IR spectroelectrochemistry carried out by Osella et al. showed that the radical Co(CO)\textsubscript{4}\textsuperscript{−} could recombine with the [Co(CO)\textsubscript{2}(ethynylestradiol)]\textsuperscript{−} radical to regenerate almost quantitatively the parent complex. No such process was observed for these systems. Rapid poisoning of the electrodes due to adsorption of the electroactive species prevented further analysis.
3.5.5 Steady state photolysis and quantum yield of CO loss

For all complexes under investigation, steady state photolysis of the dicobalt complexes in the presence of a trapping ligand, PPh$_3$, resulted in CO loss and formation of the triphenylphosphine trapped pentacarbonyl and tetracarbonyl species ([($\mu_2$-alkyne)Co$_2$(CO)$_5$(PPh$_3$)] and ([($\mu_2$-alkyne)Co$_2$(CO)$_4$(PPh$_3$)$_2$]).

Photosubstitution occurred following photolysis at $\lambda > 520$ nm albeit in minor amounts. Irradiation at $\lambda > 410$ nm caused increased formation of the pentacarbonyl photoproduct. However irradiation at $\lambda > 320$ nm resulted in a significant amounts of both the pentacarbonyl and tetracarbonyl photoproduct.

Subsequently, the quantum yield of CO loss was calculated at various wavelengths to investigate the wavelength dependence of the photochemical process. The quantum yields of CO loss were determined at 313, 365, 405 and 546 nm for PhCCPh-Co$_2$(CO)$_6$, ThCCPh-Co$_2$(CO)$_6$ and FeCCH-Co$_2$(CO)$_6$.

The UV-vis absorbance spectra for all three hexacarbonyl complexes show an intense absorbance in the UV region up to 370 nm with two broad low intensity absorbanes in the visible region extending to 600 nm (to 750 nm for FeCCH-Co$_2$(CO)$_6$). Photolysis of all three complexes resulted in minor growth of a new absorbance in the range 380 – 420 nm which indicated photosubstitution of a carbonyl ligand with a triphenylphosphine moiety was occurring.

The mean values of all quantum yield experiments are given in table 5 and summarised in figure 32. The results show that the photochemical quantum yield of CO dissociation was dependent on the excitation energy. The quantum yield of CO loss was highest when the sample was irradiated at high energy ($\lambda_{exc} = 313$ nm and $\lambda_{exc} = 365$ nm) where the complexes possess strong $\pi-\pi^*$ absorbance bands. At 405 nm, the UV-vis spectra of all three complexes display only small absorbance bands and all quantum yields were found to be less than 5% at this wavelength. However the quantum yield increased with $\lambda_{exc} = 546$ nm. The CO loss process ranged from 5 – 23%. This was unexpected given that the absorbance bands at 546 nm are weaker transitions than those at 405 nm. Importantly the
quantum yield decreased on going from 546 nm to 405 nm, but increased on going from 405 nm to 365 nm to 313 nm.

At all wavelengths \textit{PhCCPh-Co}_2(\textit{CO})_6 possessed the lowest quantum yield for CO loss (3 – 8 %) which may indicate that this complex is more stable towards photosubstitution reactions. CO loss quantum yields for \textit{ThCCPh-Co}_2(\textit{CO})_6 were in the range 4 – 15 % while \textit{FeCCH-Co}_2(\textit{CO})_6 showed the highest quantum yields (5 – 23 %), except at 365 nm where \textit{ThCCPh-Co}_2(\textit{CO})_6 produced slightly more of the trapped pentacarbonyl photoproduct. The high quantum yield and hence facile nature of CO loss in the ferrocenyl complex may be due to less steric hindrance within the complex as there is only one substituent on the ethynyl bridge.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{quantum_yield_graph.png}
\caption{Results of quantum yield experiments for CO loss in \textit{PhCCPh-Co}_2(\textit{CO})_6 (blue diamond), \textit{ThCCPh-Co}_2(\textit{CO})_6 (red square) and \textit{FeCCH-Co}_2(\textit{CO})_6 (green triangle).}
\end{figure}
3.5.6 Picosecond time resolved infrared studies

Experimental evidence for the accepted mechanism of the PKR has been limited. Laser flash photolysis with UV-vis detection and matrix isolation studies with IR detection suggested two possible photochemical pathways for \((\mu_2\text{-alkyne})\text{Co}_2(\text{CO})_6\) complexes following excitation. Irradiation at \(\lambda_{\text{exc}} = 355\text{ nm}\) resulted in Co-Co bond homolysis with \(\tau_{\text{recomb.}} = 25\text{ ns}\),\(^{41}\) while irradiation at \(\lambda_{\text{exc}} = 254\text{ nm}\) in an argon matrix resulted in reversible CO loss. More recently Gibson et al. reported that Co-Co cleavage competes with CO loss and alkene binding in an (alkyne)(binap)tetracarbonyl dicobalt complex (binap = 2,2’-bis(diphenylphoshino)-1,1’-binaphthyl) and that cobalt-cobalt bond cleavage was a facile process.\(^{45}\) TRIR spectroscopy has not been used to investigate the photochemistry of \((\mu_2\text{-alkyne})\text{Co}_2(\text{CO})_6\) type complexes. Thus, picosecond time resolved infrared spectroscopy was used to probe the photochemistry of three \((\mu_2\text{-alkyne})\text{Co}_2(\text{CO})_6\) complexes.

As discussed previously the UV-vis absorbance spectra of the complexes investigated, \(\text{PhCCPh-Co}_2(\text{CO})_6\), \(\text{ThCCPh-Co}_2(\text{CO})_6\), and \(\text{FcCCH-Co}_2(\text{CO})_6\), display a \(\pi-\pi^*\) transition with ligand field character at \(< 280\text{ nm}\), in addition to a band at approximately 350 nm and two weak bands in the range 380 – 730 nm which were attributed to metal to ligand charge transfer transitions (Fig. 33). Molecular orbital calculations were carried out by Hoffmann et al.\(^{68}\) on \((\mu_2\text{-alkyne})\text{Co}_2(\text{CO})_6\) complexes at the Hückel level and demonstrated that in the perpendicular isomer, the HOMO \(a_2\) level corresponded to alkyne-to-metal back-bonding, while the HOMO-1 \(a_1\) level corresponded to a Co-Co bond. The LUMO \(b_2\), and LUMO+1 \(b_1\) levels are antibonding with respect to the alkyne-to-metal bonds. These results are in agreement with \textit{ab initio} molecular orbital calculations reported by Van Dam et al.\(^{69}\) Photoelectron spectroscopy subsequently confirmed the relative order of the bonding orbitals proposed using molecular orbital calculations.
Figure 33  Overlay of the absorbance spectra of \textit{PhCCPh-Co_2(CO)_6} (blue line), \textit{ThCCPh-Co_2(CO)_6} (green line), and \textit{FeCCH-Co_2(CO)_6} (red line) recorded in pentane. Spectra have been normalised at their $\lambda_{\text{max}}$.

Photoexcitation ($\lambda_{\text{exc}} = 400$ nm, $\tau_{\text{FWHM}} = 150$ fs) of all three complexes resulted in depletion of the ground state $\nu$(CO) bands of the complex, together with the generation of three new bands in the carbonyl region within the laser pulse (Table 7). The initial IR bands corresponded to a vibrationally hot species and the bands shifted to higher wavenumber over 10 ps. Vibrational cooling was observed for all three complexes and has been observed previously on a ps timescale as reported by Vlček et al. for a number of metal carbonyl systems.\textsuperscript{70} These vibrationally cooled bands then decay with complete recovery of the initial bleaches. The lifetimes of the transient species was calculated to be in the range 38 - 71 ps. All three complexes in this study displayed similar spectral changes (Table 7, Fig. 25-27) and the kinetics were largely solvent independent (Table 8).
<table>
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<th>CH₃CN</th>
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</tr>
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<tr>
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<td></td>
<td></td>
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<tr>
<td>FeCCH-Co₂(CO)₆</td>
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<tr>
<td>Parent bands</td>
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<td>2089, 2050, 2022</td>
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<td>2080, 2046, 2009</td>
<td>2084, 2046, 2007</td>
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*Table 7* Observed IR stretching frequencies following excitation at 400 nm in CH₃CN, THF and pentane.

<table>
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<th>Complex</th>
<th>CH₃CN</th>
<th>THF</th>
<th>Pentane</th>
</tr>
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<tr>
<td>PhCCPh-Co₂(CO)₆</td>
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<td>70</td>
<td>71</td>
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<tr>
<td>ThCCPh-Co₂(CO)₆</td>
<td>63</td>
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<td>---</td>
</tr>
<tr>
<td>FeCCH-Co₂(CO)₆</td>
<td>50</td>
<td>38</td>
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</table>

*Table 8* Lifetimes, following vibrational cooling, of transient species produced following 400 nm excitation of complexes PhCCPh-Co₂(CO)₆, ThCCPh-Co₂(CO)₆ and FeCCH-Co₂(CO)₆.
To discount the possibility of the observed bands belonging to a solvent pentacarbonyl species, $(\mu_2\text{-alkyne})\text{Co}_2(\text{CO})_5(\text{solvent})$, triphenylphosphine was added to a solution of $\text{FcCCH-Co}_2(\text{CO})_6$. However excitation at 400 nm and also at 532 nm showed no new bands on the nanosecond time scale in the TRIR experiments that could be assigned to $\text{FcCCH-Co}_2(\text{CO})_5(\text{PPh}_3)$. This is in contrast to steady state photolysis, where in the presence of PPh$_3$, the monosubstituted complex, $\text{FcCCH-Co}_2(\text{CO})_5(\text{PPh}_3)$, and subsequently the disubstituted complex $\text{FcCCH-Co}_2(\text{CO})_4(\text{PPh}_3)_2$ formed with bands observed at 2062, 2011 and 2004 cm$^{-1}$ and 1989, 1971 and 1966 cm$^{-1}$ respectively (appendix H).

Conventional electron counting in organometallic chemistry implies that the cobalt compounds discussed throughout this chapter should have a Co-Co single bond, however, a recent charge density study on the bonding interactions in $(\text{HC}≡\text{CC}_6\text{H}_{10}\text{OH})\text{Co}_2(\text{CO})_6$, indicates that the Co-Co bonding is weak and a singlet diradical character is proposed for this compound.$^{71}$ An earlier theoretical study by Platts et al. also proposed that the more appropriate designation for $(\mu_2\text{-C}_2\text{H}_2)\text{-Co}_2(\text{CO})_6$ is that of a singlet diradical, where the ground state electronic structure has a partial occupation of both Co-Co bonding and antibonding orbitals.$^{23}$

Quantum chemical calculations (B3LYP/LANL2DZ+p) were carried out$^{72}$ and provided a model for transient species following photoexcitation of $(\mu_2\text{-alkyne})\text{Co}_2(\text{CO})_6$ complexes and predicted IR spectra of possible intermediate species (Table 9 and Appendix I). The IR properties of $(\mu_2\text{-alkyne})\text{Co}_2(\text{CO})_6$ on both the singlet and triplet ground state surfaces were calculated. It was apparent that on moving from the singlet to the triplet surface the $\nu(\text{CO})$ bands of the model complex, $(\mu_2\text{-C}_2\text{H}_2)\text{Co}_2(\text{CO})_6$, move to lower energy. In fact, the transient $\nu(\text{CO})$ bands observed in the TRIR experiments were all at lower energy compared to the parent bands (Fig. 25-27, Table 7). In addition, the calculated Co-Co bond length increases from 2.47 Å on the singlet surface (equal to twice cobalt’s covalent radius of 1.25 Å) to 3.10 Å for the triplet species. This suggests that the Co-Co interaction is considerably weaker in the triplet state.
Thus, combined picosecond TRIR studies and theoretical calculations allowed for the identification of the radical species generated following excitation of $(\mu_2$-$C_2H_2)Co_2(CO)_6$ complexes. The data indicate the formation of a triplet diradical species. Therefore, the transient species observed in the TRIR experiments was assigned to the $^3(\mu_2$-alkyne)$Co_2(CO)_6$ diradical species, generated by rapid Co-Co bond homolysis with subsequent recombination to form the parent complex.

The observation of a triplet species in the picosecond TRIR experiments requires fast intersystem crossing from the singlet excited state on the order of $1 \times 10^{12}$ s$^{-1}$. While this is fast, it is not without precedence in the literature.$^{74,75}$ Other possibilities for the species observed that were considered include: the isomer in which the alkyne lies parallel to the Co-Co bond, a species where one Co-alkyne bond is cleaved, and a Co→CO charge transfer excited state. Hoffmann found that the parallel isomer lies 2.5 eV higher in energy than that of the perpendicular isomer. As the TRIR experiments carried out at $\lambda_{exc} = 532$ nm produced transient species identical to those observed following 400 nm excitation, the possibility of the parallel isomer can be ruled out based on energetic arguments. However, as these studies were carried out over 25 years ago, further theoretical studies were preformed to rule out the possibility of involvement of the parallel isomer in the complexes under investigation.$^{72}$ DFT methods were used in an attempt to calculate the energy difference between the two isomeric forms, though, repeated attempts to locate the parallel isomer at the minimum on the singlet potential energy surface failed. It was concluded that the parallel isomer did not play a

<table>
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<td>Observed</td>
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<td>Singlet</td>
<td>2097.9 2051.3 2037.6 2035.1 2012.7</td>
</tr>
<tr>
<td>Triplet</td>
<td>2087.5 2057.9 2024.1 2021.7 2015.2</td>
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</table>

Table 9 Observed and calculated singlet and triplet state spectra for $(\mu_2$-$C_2H_2)Co_2(CO)_6$. A correlation factor of 1.0222 was used to correct the calculated $v_{(CO)}$ bands of the ground state triplet species.$^{73}$
significant role in the photochemistry of the \textbf{PhCCPh-Co}_2(\text{CO})_6, \textbf{ThCCPh-Co}_2(\text{CO})_6 and \textbf{FcCCH-Co}_2(\text{CO})_6 complexes. An intermediate arising from cleavage of the Co-C alkyne bonds was also excluded based on the number of IR bands observed. Although a Co-to-CO charge transfer excited state should be considered, the most likely explanation for the short lived species is that of the triplet diradical based on the results proposed here.

There was no evidence of the CO loss photoproduct in the TRIR experiments following excitation at 400 nm and 532 nm. Addition of a molar excess of trapping ligand to a sample of \textbf{FcCCH-Co}_2(\text{CO})_6 produced TRIR spectra practically identical to that without the trapping ligand. The quantum yield experiments revealed, CO loss for the three complexes \textbf{PhCCPh-Co}_2(\text{CO})_6, \textbf{ThCCPh-Co}_2(\text{CO})_6 and \textbf{FcCCH-Co}_2(\text{CO})_6 was low at 405 nm. The quantum yield for CO loss was less than 5\% at this wavelength, which was close to the excitation wavelength used for TRIR experiments (400 nm). It is unlikely that a photoprocess with such a low quantum yield would be observed in the TRIR experiments.

The quantum yield for CO loss varied with excitation wavelength. At 546 nm the quantum yield for CO loss was 5 – 23\%. It is unlikely that the low quantum yield photoprocesses (\(< 10\%\)) would be observed, thus the TRIR experiments are in good agreement with the quantum yields obtained for \textbf{PhCCPh-Co}_2(\text{CO})_6 and \textbf{ThCCPh-Co}_2(\text{CO})_6. However, the quantum yield for CO loss in \textbf{FcCCH-Co}_2(\text{CO})_6 was 23\%. No evidence for the CO loss photoproduct was observed. This is a genuinely puzzling aspect of the results and the experiments will need to be repeated if an opportunity arises.

The diagrammatical representation below (Fig. 34) shows the photophysical processes that occur following excitation. Following 400 nm pulsed excitation the (\(\mu_2\)-alkyne)Co_2(\text{CO})_6 complex absorbs light and is excited to its singlet excited state, rapid intersystem crossing to the triplet state occurs. Following this Co-Co bond homolysis and recombination occurs followed by full recovery of the ground state. However, continuous wave irradiation (\(\lambda\_\text{exc} = 546\ \text{nm}\)) resulted in CO loss as shown below.
Co-Co bond homolysis and recombination followed by relaxation to the ground state

**Figure 34** Diagrammatical representation of the photophysical processes that occur following 400 nm pulsed irradiation and 546 nm continuous wave (C.W.) irradiation.

Thus, combined picosecond TRIR studies and theoretical calculations allowed for the identification of the radical species generated following excitation of ($\mu_2$-alkyne)Co$_2$(CO)$_6$ complexes. The data indicate the formation of a triplet diradical species that rapidly recombined to regenerate the parent complex in all cases (Scheme 6). Lifetimes for the triplet diradical species were in the range 38 – 71 ps.$^{51}$

**Scheme 6** Co-Co bond homolysis and recombination following 400 nm excitation.

R$_1$ = Phenyl or ferrocene, R$_2$ = H, phenyl or thiophene
3.6 Conclusions

In this chapter experimental work concerning the excited state dynamics of linear organic molecules and their organometallic counterparts has been presented. Ligands, NB-L1 and NB-L5 – NB-L7 were used to investigate the effect of terminal group substitution on the organic moiety, with respect to their absorbance, emission and electrochemistry. The results showed that the attachment of an electron withdrawing moiety to the organic ligand resulted in bathochromic shifts in the absorbance spectra. The non-fluorescent NB-L1 became weakly fluorescent upon terminal substitution, the intensity of the emission increased with increasing electronegativity of the terminal substituent and in conjunction with this the fluorescent lifetimes of the molecules were increased also. Electrochemistry showed that thienyl molecules become more stable when an electron withdrawing group was attached due to increased electron delocalisation within the molecules.

Steady state photolysis carried out in the dicobalt hexacarbonyl complexes resulted in CO loss and quantum yields for the CO loss process indicated that the photochemical process was wavelength dependant. The photochemical activation of (µ2-alkyne)Co₂(CO)₆ complexes was studied by ps-TRIR and combined theoretical calculations allowed for the identification of the formation of a triplet diradical species that rapidly recombined to regenerate the parent complex. Lifetimes for the triplet diradical species were in the range 38 – 71 ps.
3.7 Bibliography


Theoretical calculations were carried out by Prof. C. Long at Dublin City University.


Chapter 4

The synthesis and photochemistry of freebase and zinc monopyridyl porphyrins and the corresponding metal carbonyl porphyrin complexes.

Chapter four commences with literature survey focusing on the photophysics of pyridyl porphyrins and related organometallic systems. The aims and objectives of the chapter are discussed. The synthesis of the monopyridyl porphyrin and metal carbonyl derivatives produced for this study is then described. The photochemistry of the complexes was examined by pump and probe TRIR spectroscopy on a picosecond timescale.
4.1 Literature Survey

4.1.1 Introduction to pyridyl porphyrins

Porphyrin metal complexes have found great use in photosynthetic research. From the first man made porphyrins to the supramolecular arrays of today, porphyrins and related macrocycles have been studied for their electron transfer and energy transfer potential. Systems that undergo electron transfer processes from porphyrins to externally but covalently linked transition metal complexes have been extensively studied since the mid nineties. Among supramolecular systems, those that contain a porphyrin coordinated to a peripheral transition metal are of particular interest as these arrays can mimic the electron or energy transfer processes observed in photosynthesis. Pyridyl porphyrins are particularly attractive building blocks for the construction of photoactive supramolecular systems. The structures shown in figure 1 display a variable number of 4-pyridyl ($n$) and phenyl ($4 - n$) groups at the meso position(s) of the porphyrin macrocycle. As with all porphyrins, these mixed pyridyl/phenyl porphyrins have attractive spectroscopic, photophysical and redox properties. In addition, the meso pyridyl groups provide great synthetic flexibility as the peripheral nitrogen atom(s) can be coordinated to metal complexes of various coordination numbers and geometries. Complexation at the peripheral pyridyl nitrogen provided a simple route to a new class of porphyrins. The meso pyridyl group can act as a ligand for metal sites that are held at a fixed distance and angle to the porphyrin macrocycle.
Figure 1

Five 4-pyridyl (n) and phenyl (4 - n) meso substituted porphyrins.
4.1.2 Porphyrins coordinated to metal carbonyls.

Coordination of a metal carbonyl to a porphyrin allows the study of the extent of electron or energy transfer between the two units using the extensive data for the excited states of the individual porphyrin and metal carbonyl fragments. Various porphyrins have been coordinated to transition metal carbonyls including (µ-H)-Os(CO)$_{10}$, Re(CO)$_3$Cl, RuCl$_2$(DMSO)$_2$CO, Cr(CO)$_3$ and W(CO)$_5$ some of which are discussed below. However only a few of these system have had their photochemistry examined.

Mono and disubstituted pyridyl porphyrins (1 - 3, Fig. 2) were treated with an excess of Os$_3$(CO)$_{10}$(NCMe)$_2$ to give triosmium cluster complexes (4 - 6, Fig. 2). In complex 4, the pyridyl ring of the porphyrin was orthometallated and bridged one edge of the Os$_3$ triangle. This afforded a four membered ring containing Os, Os, C and N with a hydride ligand bridging one Os-Os edge. Complex 5 was isostructural with complex 4. The coordinated clusters of complex 6 can be $cis$ or $trans$ to one another (relative to the porphyrin plane). The absorbance spectra of 4 - 6 were similar to the uncomplexed pyridyl porphyrins 1 – 3, except for a blue shift of the Soret band by 4, 3 and 7 nm respectively and an increase in absorbance between 220 and 420 nm where the cluster absorbance bands were evident. The fluorescence spectra intensities and excited state lifetimes of 4 - 6 were somewhat quenched compared to 1-3. The fluorescence lifetimes were 0.76, 0.70, 0.76, 0.30, 0.37 and 0.21 ns for 1 - 6 respectively. Fluorescence quenching was attributed to the heavy atom effect arising from the metal cluster rather than energy- or electron-transfer processes between the cluster and the porphyrin.
Sullivan and co-workers synthesised 7 (Fig. 3) in which a labile triflate group was replaced by a pyridine ligand. Subsequently osmium exclusively bound to the exterior of a porphyrin through direct coordination of the pyridyl linkage was reported by Hyslop et al. H$_2$8 (Fig. 3) was prepared via a modified version of this method and metallated with zinc (Zn8, Fig. 3). MPyTPP, ZnTPP and 7 were used as model compounds to delineate the effect of coordination of the Os unit onto the pyridyl porphyrin. Comparisons of the electrochemical redox properties of H$_2$8 to MPyTPP and Zn8 to ZnTPP showed only minor shifts in both the osmium and porphyrin potentials indicating that the ground states were unperturbed in the dyads. With regard to the model 7, incorporation of the CO unit onto the osmium metal centre caused a blue shift of the MLCT absorbance band so that it occurred at the same energy as the Soret band of MPyTPP ($\lambda_{\text{max}} = 417$ nm).
bipyridine $\pi$-$\pi^*$ bands of $\text{H}_2\text{8}$ and $\text{Zn8}$ (~290 nm) were separated from the porphyrin Soret and Q bands thus permitting preferential excitation of the Os portion of the molecule. The emission maximum of 7 ($\lambda_{em} = 590$ nm) overlapped with the Q band absorbance of MPyTPP (590 nm) and ZnTPP (586 nm) thus creating an ideal system for energy transfer. UV-vis spectra of the complexes $\text{H}_2\text{8}$ and $\text{Zn8}$ were not simple superpositions of the parent 7 and MPyTPP or ZnTPP respectively. Complexation of the porphyrin to osmium resulted in the addition of a bipyridine $\pi$-$\pi^*$ transition in the UV region while the Soret and Q bands in both the freebase and zinc porphyrins were broadened, decreased in intensity and red-shifted with respect to the model porphyrins (Table 1), which indicated electronic coupling. Excitation of the porphyrin dyads, $\text{H}_2\text{8}$ and $\text{Zn8}$, was carried out at 260 nm (osmium based bipyridine $\pi$-$\pi^*$ transition) and at 420 nm (porphyrin Soret band). Excitation of $\text{H}_2\text{8}$ at 420 nm resulted in emission at 659 nm, a red shift of 8 nm compared to MPyTPP with a decrease in intensity by a factor of 5. Excitation at 260 nm gave similar results with the emission bathochromically shifted and a similarly decreased in intensity. The decrease in emission intensity was typical of the heavy atom effect. The red shifted absorbance and emission maxima for $\text{H}_2\text{8}$ and lack of change in electrochemical potentials suggested that the ground state energies of the porphyrin unit remained the same while the excited state energies were lowered by the attachment of the Os group. Emission occurred only from the porphyrin moiety of $\text{H}_2\text{8}$ regardless of excitation wavelength, indicating that energy transfer from the osmium group to the porphyrin occurred. The metallated derivative, $\text{Zn8}$, produced different results. Model compounds, ZnTPP and ZnMPyTPP, possess almost identical emission spectra with two bands at 598 and 648 nm, the latter more intense than the former. Excitation of $\text{Zn8}$ at 460 nm yielded a bathochromically shifted (17 nm) and significantly quenched (by a factor of 11) fluorescence spectrum in which the higher energy band was the most intense. Some quenching of the emission was attributed to the heavy atom effect however additional quenching processes were considered as the total quenching was nearly three times higher than that of the freebase derivative. The authors suggested that the almost complete quenching and change in profile of the emission when the Os bipyridine moiety of $\text{Zn8}$ is excited supports the occurrence of electron transfer.
Table 1 Photophysical data for osmium porphyrin assemblies and model compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>Soret FWHM (cm$^{-1}$)</th>
<th>$\lambda_{\text{em}}$ (nm)</th>
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<tr>
<td>7</td>
<td>262, 302, 422</td>
<td></td>
<td>589</td>
</tr>
<tr>
<td>H$_2$8</td>
<td>260, 302, 423, 518, 57, 592, 649</td>
<td>1340</td>
<td>659</td>
</tr>
<tr>
<td>Zn8</td>
<td>251, 261, 302, 425, 552, 596,</td>
<td>1320</td>
<td>614</td>
</tr>
<tr>
<td>MPyTPP</td>
<td>417, 514, 548, 590, 645, 690</td>
<td>690</td>
<td>651</td>
</tr>
<tr>
<td>ZnTPP</td>
<td>419, 548, 586</td>
<td>570</td>
<td>597</td>
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Pyridyl porphyrins functionalised with Re(CO)$_3$Cl resulted in the formation of porphyrin dimers (9 and 10, Fig. 4). The dimers featured a rigid co-planar geometry for the donor and acceptor chromophores via coordinative assembly. Thus the rigidity of the compounds provided an efficient geometry for singlet energy transfer and made them candidates for both through-bond and through-space energy transfer. The porphyrin dimers consist of homodimers (9\textit{a} and 9\textit{b}, Fig. 4) and mixed dimers (9\textit{c}, Fig. 4). The porphyrin Soret band was broadened and reduced in intensity upon incorporation into dimers indicating slight electronic coupling in this region while the Q band region was the sum of the individual zinc and freebase monomers indicating little or no electronic coupling. Consistent with coordination to Re(I), the absorbance and fluorescence maxima were red shifted by 8 – 10 nm with respect to the monomer porphyrins. Singlet lifetimes and quantum yields were typical of singlet porphyrin emission with the freebase porphyrin complexes more emissive than their zinc analogues. Despite complexation with rhenium the assemblies remained fluorescent. However, a 75 % decrease in emission quantum yield upon dimer formation was observed and ascribed to heavy atom effect. Similar to other studies on Zn-Fb porphyrin pairs, dimers 9\textit{c} and 10\textit{c} displayed efficient singlet energy transfer from the zinc porphyrin to the freebase porphyrin. Excitation of the Soret region resulted in significantly reduced emission from the zinc component of 9\textit{c} and enhanced emission from the freebase component. Steady state fluorescence studies of 9\textit{c} and 10\textit{c}, using the respective symmetric dimers as reference compounds gave energy transfer rate constants of 1.3 x $10^{10}$ and 9.7 x $10^9$ s$^{-1}$. This was similar to rate constants observed for organic Zn-Fb porphyrin dimers in which aromatic spacers were implicated for EnT mediation$^6$ and faster than closely related assemblies in which through-space EnT dominated.$^7$ In these systems the structured rigidity and enforcement of donor-acceptor coplanarity for both 9\textit{c} and 10\textit{c} could enhance either pathway.
Metal carbonyls have also been used to create porphyrin squares such as 11 (Fig. 5). 8 5,15-meso-pyridylporphyrins were used as bridging ligands and Re(CO)₃Cl moieties were used as corners to form molecular squares, while porphyrin metallation provided a basis for single or multipoint guest binding via axial ligation. Square formation induced a ~6 nm red shift in the porphyrin Soret band which is consistent with net removal of electron density from the porphyrin π system upon complexation. Near-UV fluorescence (MLCT region) indicated that the metal corners have a structural role rather than a photophysical role within the framework. Complexes remained luminescent but with fluorescence generated from porphyrin localised excited states, lifetimes of 3.0 and 2.4 ns were observed for H₂11 and Zn₁₁. Addition of pyridine to Zn₁₁ led to a significant bathochromic shift in the fluorescence, a response not observed for H₂₁₁, clearly demonstrating axial ligation of the porphyrin bound zinc by pyridine. Thus the molecular square can be used in host-guest complex construction.

Figure 4 Pyridyl porphyrin dimers functionalised with Re(CO)₃Cl.
Compounds containing a \([\text{fac-Re(CO)}_3\text{(diimine)}]^+\) unit are electron acceptors and in solution display intense luminescence in the visible region due to a long lived \(\text{Re-}\pi^*(\text{diimine})\) MLCT excited state. There are two ways that \([\text{fac-Re(CO)}_3\text{(diimine)}]^+\) can be connected to a porphyrin: the porphyrin can act as a ligand through a peripheral \(\text{meso}\) pyridyl group and is bound directly to the Re(I) centre adjacent to the coordinated diimine or the diimine is functionalised and then conjugated to a peripheral group on the porphyrin (in this case the coordination sphere of Re(I) must be completed by a sixth ligand, either neutral or anionic).

Casanova et al. synthesised porphyrin-Re(I) conjugates of the first type, where the pyridyl porphyrin was directly coordinated to the Re(I) electron-acceptor fragment, \([\text{fac-Re(CO)}_3\text{(diimine)}]^+\). Assemblies contained either 4-pyridyl \(\text{meso}\) porphyrins which were mono or tetra substituted (12 and 13, Fig. 6) or 3-pyridyl systems (14 and 15, Fig. 6) and the porphyrins were also metallated with zinc(II). Apart from minor red shifts in the absorbance spectra with respect to the corresponding uncomplexed porphyrin, the spectra
of 12 - 15 were the summation of the molecular components, indicating that interaction between the porphyrin and rhenium was weak. All were dominated by the porphyrin Soret band with Q bands ranging from 500-700 nm. The Re(bpy) unit did not absorb appreciably above 350 nm and the Re→bpy MLCT transition (\(\lambda = 350\) nm) was obscured by the porphyrin Soret band. The porphyrin-Re(I) conjugates possessed typical porphyrin-based fluorescence with a small shift in relation to ZnTPP. A moderate but significant decrease of the emission intensity and lifetime is observed for Zn12 and the effect was more pronounced for the pentad Zn13. In general the porphyrin fluorescence was affected but not strongly quenched by the presence of the peripherally bound rhenium unit(s). Possible mechanisms for the quenching observed were (a) electron transfer quenching and (b) the heavy atom effect. The emission for Zn12 and Zn15 were further investigated in the presence of pyridine. A marked shortening in the lifetime of Zn12 (from 900 ps to \(~250\) ps) with a proportional decrease in the emission intensity was observed. Excitation in the UV region where the rhenium(I)bpy absorbed did not produce MLCT emission clearly indicating that its triplet state was efficiently quenched in all compounds. The authors concluded that the heavy atom effect was the cause of fluorescence quenching as it was more efficient for pentameric than dimeric species. Nanosecond time resolved absorbance spectroscopy of the Zn(II)porphyrin-Re dyads showed decay of a transient for Zn12 with a lifetime of > 20 \(\mu\)s that corresponded to the triplet state. Ultrafast spectroscopy, with 560 nm excitation, was also carried out. The initial spectrum for Zn12 taken after the laser pulse (1 ps) displayed typical zinc porphyrins \(S_1\) features and evolved to a final spectrum practically identical to that of the nanosecond laser experiment which corresponded to the triplet state. The singlet excited state spectrum evolved to that of the triplet over \(~1\) ns. The ultrafast experiments were then repeated in the presence of pyridine. The temporal spectral changes observed were substantially different than that observed in the absence of pyridine, with a biphasic behaviour taking place for \(t \leq 80\) ps and \(t \geq 80\) ps. A time constant of 20 ps was obtained for the first process at 618 nm and 300 ps for the second process at 585 nm. The final spectrum recorded at 1000 ps was almost identical to the triplet spectrum observed in the nanosecond experiments. This biphasic behaviour was consistent with a charge separated state (ZnPorph\(^+\) - Re(bpy)\(^-\)) which was sufficiently close in energy to the singlet state \(S_1\) to allow fast equilibrium between them. In the presence of pyridine the processes that occurred were (a) an electron transfer process from the singlet of the zinc-porphyrin to the Re(bpy) fragment, with a time
constant of 20 ps, which led to a charge separated state and (b) the equilibrium mixture of singlet and charge separated states that decayed to the triplet state in 300 ps.

Complexes of the type [Re(CO)_3(bpy)L]^n (n = 0, +1) with a metalloporphyrin covalently linked to the rhenium unit, have also been synthesised (16 – 20, Fig. 7) and their photochemistry and electrochemistry were examined. UV-vis spectra were dominated by the porphyrin absorbance bands. The Re-(bpy) MLCT band anticipated in the range 350 – 420 nm was masked by the porphyrin Soret band. Time resolved absorbance studies (10 ns laser pulse, 355 nm excitation) were carried out. The absorbance spectra of the parent porphyrin, 20, and porphyrin complex, 17, were characteristic of the porphyrin \( ^3(\pi-\pi^*) \) excited state. There was no evidence of excited state absorbance due to Re → bipyridylporphyrin MLCT transitions, most likely because these bands were weak in
comparison to the porphyrin transient bands observed. Transient species of 20 and 17 decayed with lifetimes of $\tau = 2 \times 10^{-5}$ s and $\tau = 3 \times 10^{-6}$ and respectively. The emission spectrum observed for the porphyrin complex 17 was typical of metalloporphyrins with peaks at 606 and 656 nm. Emission intensity was 50 % lower than that of 20. Emission from the $^3$MLCT excited state of Re(CO)$_3$(bpy)Br is observed at 620 nm and time resolved emission from the $^3$MLCT excited state of Re(CO)$_3$Br(bpy) was observed (in the range 580-670 nm) with a lifetime of 63 ns. No emission was detected in this region for 17 which indicated that emission was quenched by the metalloporphyrin chromophore. Quenching of the steady state fluorescence of 20 also indicated an excited state interaction.

![Figure 7](image)

16*: [M] = [fac-Re(CO)$_3$(3-Me-Py)]$^+$
17: [M] = [fac-Re(CO)$_3$Br]
18*: [M] = [fac-Re(CO)$_3$(THF)]$^+$
19*: [M] = [fac-Re(CO)$_3$(PrCN)]$^+$
20: [M] = no rhenium moiety

Figure 7 Rheniumtricarbonyl units covalently linked to metalloporphyrins

In a subsequent study, photolysis of 16$^+$ with $\lambda > 495$ nm in the presence of triethylamine revealed that a new metal carbonyl complex was formed. Comparison of the IR spectrum with [Re(CO)$_3$(bpy)(THF)]$^+$ indicated that the axial ligand was displaced by the solvent to yield the THF complex 18$^+$. Repeating the photoreaction with excess bromide and triethylamine resulted in the formation of complex 17. Both these reactions produced 18-
electron products; however photolysis in the presence of a trace quantity of free 3-Me-pyridine produced IR features indicative of the radical 16· (Table 2). Evidence for a rhenium bipyridine based radical, either 16· or 19·, was obtained by EPR and IR spectroscopy following photolysis of 16+ with triethylamine and excess 3-Me-pyridine in PrCN as well as the cationic solvent complex 19+. The authors suggested that the porphyrin acted as a sensitiser upon visible light excitation and product formation depended on electron transfer from triethylamine. As a control, complex 21 without the porphyrin unit was synthesised. Photolysis (λ > 495 nm) of 21+ in THF in the presence of Et3N yielded no product. Spectroelectrochemistry with UV-vis detection showed the reversible oxidation of 16+ and 17 was based on the porphyrin moiety and occurred at the same potential as that of 20 and ZnTPP (380 mV vs. Fe/Fe+ in THF). IR detection indicated that the reduction observed in CV occurred on the rhenium bipyridine site for both 16+ and 17. The reduction waves were different from the simple models, 21+, [Re(CO)3(bpy)Br] and from 20. Reduction of 16+ resulted in three new IR bands at 161, 1892 cm⁻¹ and was assigned to 18+, whereas reduction at low temperature (223 K) in butyronitrile gave bands at 1910, 1903 and 1893 cm⁻¹ consistent with the radical species 16·. Thus reduction of 16+ occurred at the Re-(bpy) site whereas reduction of 20 occurred at the porphyrin. As no ligand substitution occurred without reduction, the radical 16· was the species that underwent substitution. On reduction of 16+ in the presence of bromide ions, the 3-Me-pyridine was displaced by bromide and the radical anion 17· formed, was then reoxidised to compound 17 quantitatively. Analogue 20, without Re was effectively photoreduced by triethylamine to the porphyrin radical anion 20·−, reiterating that triethylamine can transfer an electron to the excited state of the porphyrin. Intramolecular electron transfer occurred with a driving force of -0.25 eV and ca. 0.06 eV for 16+ and 17 respectively. Despite this similarity, 17 did not undergo photochemical reduction under the same conditions as 16+. It was reduced at more negative potential than 16+ and an irreversible reduction wave was observed in THF. It was possible to displace an axial ligand in 17 by THF during reduction and subsequent reoxidation gave the cationic THF complex 18+. Thus the introduction of the pyridyl porphyrin into the design of 16+ induced substitution at a remote site as a result of photo-induced electron transfer.10
Complex       Solvent  ν(CO) (cm\(^{-1}\))
16⁺             THF      2031, 1927 (br)
16⁻             PrCN     2010, 1903, 1893
16             THF      2011, 1907, 1893
17             THF      2020, 1920, 1897
17⁺             THF      1998, 1888, 1868
18⁺             THF      2016, 1914, 1892
19⁺             PrCN     2038, ~1835
19             PrCN     2010, 1903(br), 1893(br)
21⁺             THF      2031, 1927(br)
21⁻             THF      2010, 1905, 1892

Table 2    CO stretching frequencies of complexes in photolysis study.

Two types of freebase and zinc tetraaryl porphyrins were synthesised (22 and 23, Fig. 8), then mono substituted with tungsten pentacarbonyl via a pyridine linker (22-W(CO)\(_5\) and 23-W(CO)\(_5\), Fig. 8).\(^{11}\) This series of porphyrins, coordinated to a single metal carbonyl unit via a pyridyl linker, was used to further investigate interactions between the two chromophores. Complexes 24 and 25 were used as model systems for comparative purposes. The UV-vis spectra were dominated by porphyrin transitions with no shift in band position observed upon peripheral metallation with W(CO)\(_5\), although a reduction in extinction coefficients of the Soret bands occurred. No tungsten based absorbances were detected for the porphyrin-W(CO)\(_5\) complexes. The MLCT bands of both 22-W(CO)\(_5\) and 23-W(CO)\(_5\) occurred in the range 390 – 400 nm (by comparison with 24 and 25) and so were overlapped by the porphyrin Soret. Luminescence studies of H\(_2\)22-W(CO)\(_5\) and H\(_2\)23-W(CO)\(_5\) revealed fluorescence spectra typical of freebase porphyrins, but the metalloporphyrins Zn22-W(CO)\(_5\) and Zn23-W(CO)\(_5\) demonstrated unusual luminescence behaviour. The emission profiles recorded immediately after preparation were typical of zinc porphyrins with two bands at 605 and 655 nm. Following longer exposure to the excitation lamp a new band was observed between the two Q band emissions at 628 nm. In the case of Zn23-W(CO)\(_5\) in THF, the third band was observed rapidly with excitation at 435 nm but not observed immediately with 556 nm excitation. Due the intensity and width of the third band the authors postulated that the extra band originated from a porphyrin based transition and tentatively suggested that it resulted from photoinduced electron transfer. Time-resolved emission (λ\(_{ex}\) > 355 nm) were carried out on H\(_2\)22 and
All four porphyrins displayed $^1(\pi-\pi^*)$ excited state emission and no difference was observed between either H$_{22}$ and H$_{22}$-W(CO)$_5$ or Zn$_{22}$ and Zn$_{22}$-W(CO)$_5$. The lifetime of the fluorescence was 22 ns for the freebase porphyrins and less than 10 ns for the zinc derivatives (width of the excitation pulse). Time resolved spectra were in agreement with steady state emission spectra in which the freebase porphyrin exhibited two fluorescence bands at 650 and 720 nm. The zinc analogues emitted at higher energy each displayed two bands at ca. 610 and 650 nm. The time resolved emission spectra of Zn$_{22}$-W(CO)$_5$ differed from Zn$_{22}$ in that it had a third emission band at 630 nm, similar to that obtained after slightly prolonged exposure to the excitation source in the steady state fluorimetry. Time resolved absorbance spectroscopy was used to probe the $^3(\pi-\pi^*)$ excited states of H$_{22}$, Zn$_{22}$, H$_{22}$-W(CO)$_5$ and Zn$_{22}$-W(CO)$_5$. Both the freebase and metalloporphyrins showed strong transient signals from 440 to ca. 480 nm with maxima at 440 nm for freebase porphyrins and at 460 nm for metalloporphyrins. The transient spectra were typical of porphyrin $^3(\pi-\pi^*)$ excited states and the presence of a W(CO)$_5$ moiety had no effect on the spectra. Reports in literature indicate transient absorbance features are observed at ca. 440-460 nm and ca. 600 nm for [(4’-X-Py)-W(CO)$_5$] (where X = electron withdrawing group). No transient feature at ca. 600 nm was observed for the porphyrin systems possibly due to the fact that at 355 nm excitation, the porphyrin sub-unit will preferentially excited. Steady state photolysis of the models, 24 and 25, and porphyrin complexes led to the formation of the same product that was readily assigned to [W(CO)$_3$(THF)] as observed by IR spectroscopy. Photolysis of H$_{22}$-W(CO)$_5$ and Zn$_{22}$-W(CO)$_5$ with $\lambda_{ex} > 395$ nm showed evidence for formation of the THF adduct. Excitation using $\lambda_{ex} > 495$ nm prevented photosubstitution as light was absorbed only by the porphyrin Q bands. As almost all the light in this excitation range ($\lambda_{ex} > 395 - \lambda_{ex} > 495$ nm) was absorbed by the porphyrin the authors postulated that tungsten based excited states were populated by energy transfer from the porphyrin moiety. The fluorescence spectra of Zn$_{22}$-W(CO)$_5$ and Zn$_{23}$-W(CO)$_5$ which exhibited an extra emission band also suggested a photochemical process occurred, most likely electron transfer.$^{11}$
Rhenium(bipyridine)(tricarbonyl)(picoline) units were then linked covalently to tetraphenylmetalloporphyrins via an amide bond between the pyridine and one phenyl substituent of the porphyrin to produce [Re(CO)$_3$(Pic)Bpy-MTPP][OTf] (26, M = Zn or Mg, Fig. 9). In the ground state UV-vis spectrum, the rhenium appended complex 26...
showed only small changes when compared to the uncomplexed porphyrin (20, M = Zn or Mg, Fig. 7). The MLCT and IL transitions expected around 370 and 300 nm were masked by the porphyrins transitions. Mg26 showed a bathochromic shift of all bands in comparison to the Zn26. The IR spectra of both porphyrin complexes displayed two bands at 2031 and 1927 cm\(^{-1}\) in THF. Steady state emission spectroscopy indicated that the zinc and magnesium porphyrins emitted strongly from the first singlet excited state. Zn26 exhibited two sharp bands at 604 and 655 nm like that of the Re free model, Zn20. Emission quantum yield was strongly affected by solvent polarity, as the solvent polarity increased the emission intensity of Zn26 was reduced compared to Zn20, to 15 % in toluene, further decreasing to 6.6 % in THF and 4.5 % in PrCN. The model Mg20 displayed two fluorescence bands at 612 and 665 nm in MeCN, the same position as Mg26 although the latter showed emission intensity only 2.5 % that of Mg20. Such dependence of quenching behaviour on solvent media is characteristic of electron-transfer processes. Energetic calculations support electron transfer from metalloporphyrin to Re(bpy) as the most likely quenching mechanism. At low temperature a reduction in quenching was observed, which supported an electron transfer mechanism.

IR spectroelectrochemistry of Zn26\(^+\) ([Re(CO)\(_3\)(Pic)-Bpy-ZnTPP]\(^+\)) in PrCN and THF was carried out. In PrCN, reduction of Zn26\(^+\) resulted in a loss of intensity of the precursor v(CO) bands at 2035 and 1933 cm\(^{-1}\) and new bands generated at 2012 and 1928 cm\(^{-1}\); the latter a very broad stretch like the corresponding band of the precursor. New bands were assigned to the radical species [Re\(^+\)(CO)\(_3\)(Pic)-Bpy\(^-\)-ZnTPP] and showed the characteristic shift to lower frequency. No significant substitution of picoline with PrCN was observed. Subsequent irreversible reduction of [Re\(^+\)(CO)\(_3\)(Pic)-Bpy\(^-\)-ZnTPP] produced a mixture of two anionic species [Re(CO)\(_3\)(PrCN)-Bpy-ZnTPP\(^-\) (major) and [Re(CO)\(_3\)Bpy-ZnTPP\(^-\)] (minor) characterised by high frequency bands at 1983 and 1948 cm\(^{-1}\), respectively, with overlapping broad low frequency bands between 1900 and 1840 cm\(^{-1}\). In THF, the reduction of [Re(CO)\(_3\)(Pic)-Bpy-ZnTPP]\(^+\) was irreversible with the parent v(CO) bands at 2033 and 1928 cm\(^{-1}\) shifting to 2011, 1906 and 1982 cm\(^{-1}\) for the corresponding radical which gradually underwent solvent exchange with a picoline moiety and produced the cation [Re(CO)\(_3\)(THF)-Bpy-ZnTPP]\(^+\) with bands at 2019, 1914 and 1897 cm\(^{-1}\). Time-resolved visible absorbance (TRVIS) spectroscopy determined the transient lifetimes of the rhenium-appended porphyrins which were reduced dramatically.
compared to their rhenium-free counterparts, but possessed identical spectral profiles. The picosecond TRVIS spectrum of $^{26}$ (M = Zn or Mg) in PrCN strongly resembled those of $^{20}$ (M = Zn or Mg) in PrCN which in turn were very similar to those of ZnTPP and MgTPP with typical porphyrin $S_1$ features of strong broad absorbance at 460 nm and stimulated emission at 610 and 660 nm. However, in harsh contrast to Zn\Mg $^{20}$, lifetimes of transient species derived from Zn\Mg $^{26}$ were much shorter, in PrCN decays with $\tau = 23.7 \pm 0.2$ ps ($Zn^{26}$) and $16.7 \pm 0.7$ ps ($Mg^{26}$) were observed. The signals decayed with first order kinetics, which were strongly solvent dependent, decaying faster in PrCN than THF. The rate of decay of the transient from Mg$^{26}$ is over two orders of magnitude greater than that of Mg$^{20}$. Nanosecond time resolved absorbance spectroscopy probed the first triplet state of the zinc porphyrins. Excitation of Zn$^{20}$ and Zn$^{26}$ in THF at 470 nm produced a transient due to the $T_1$ excited state although the transient of Zn$^{26}$ had only 6% of the intensity observed for Zn$^{20}$ and a much longer lifetime. Picosecond TRIR was used to probe charge or energy transfer in the rhenium porphyrin dyads. The TRIR spectrum of Mg$^{26}$ in MeCN, following excitation at 600 nm (Q band region) resulted in two bleaches, one sharp at 2033 cm$^{-1}$ and one broad at ca. 1931 cm$^{-1}$, due to depletion of the ground state on a sub picosecond timescale, bands were at a maximum in the first spectrum, delay 1.5 ps (Fig. 10). The bleach recovered completely with a lifetime of $34 \pm 4$ ps. Also in the initial spectrum after 1.5 ps were product bands, assigned to a charge separated state (CS), at their maximum intensity at 2008 and 1900 cm$^{-1}$ with a positive shoulder overlapping the bleach at ca. 2028 cm$^{-1}$. The CS bands closely resembled the one electron reduced species detected by IR spectroelectrochemistry. These TRIR product bands decayed with a lifetime of $20 \pm 2$ ps, revealing, after 6 ps, a pair of bands at 2023 and 1908 cm$^{-1}$, assigned to a hot ground state (HS), which in turn decayed with a lifetime of $35 \pm 8$ ps, similar to that of the recovery of the bleach. The CS state showed considerable shifts to lower frequency compared to the starting material, consistent with charge transfer from porphyrin to Re(bpy). The TRIR spectrum of Mg$^{26}$ in PrCN and following excitation at 560 and 600 nm produced decay kinetics and spectral shapes identical to those discussed above. Picosecond TRIR spectra of Zn$^{26}$ in PrCN showed bleaches at 2031 and 1932 cm$^{-1}$ formed within 1 ps of excitation (first spectrum after laser pulse, delay 1 ps) which continued to grow to a maximum after ca. 10 ps and then decayed with a lifetime of $55 \pm 8$ ps (Fig. 11). A sharp product band (labelled $\pi-\pi^*$) was observed at 2006 cm$^{-1}$ on the low energy side of the parent bleach after 2 ps with an associated band contributing to the broad maximum at 1906 cm$^{-1}$. These bands decayed over 10 ps when a
new band appeared at 2007 cm\(^{-1}\) and the low energy broad maximum shifted to \textit{ca.} 1896 cm\(^{-1}\). These CS bands reached their maximum at 10 ps and then decayed with a rate constant of 40 ± 4 ps. Product CS bands gave way to a hot species after 40 ps with maxima shifted to 2021 and 1905 cm\(^{-1}\). The decay of this third species was almost complete within 100 ps. Thus when the assemblies were excited at long wavelengths in the region where the porphyrin unit absorbed electron transfer from the porphyrin to rhenium bipyridine occurred on an ultrafast timescale. The magnesium derivative, Mg26, displayed charge separated IR bands within 1.5 ps which decayed in 20 ps while for the zinc analogue, Zn26, the charge separated IR bands rise over 5 ps and then decayed over 40 ps. The charge separated state was described as \([\text{Re}^+ (\text{CO})_3(\text{Pic})\text{Bpy}^-\text{-MTPP}^+]\) (M = Zn or Mg). When the transient state decayed a further state was identified, characterised by a reduced low frequency shift of the \(\nu(\text{CO})\) bands and assigned to a vibrationally excited ground state. The assemblies return to the initial ground state with a time constant of 35 – 55 ps. Rapid charge separation and back electron transfer provided a mechanism for quenching of the porphyrin emission that was solvent dependant.

![Diagram](image-url)

Figure 9  
\([\text{Re}(\text{CO})_3(\text{Pic})\text{Bpy}\text{-MTPP}][\text{OTf}], 26, M = \text{Zn or Mg.}\)
Figure 10  TRIR spectra of Mg\textsubscript{26} in MeCN observed following 600 nm excitation. Time delays are in ps and arrows indicate rise and decay of transients.\textsuperscript{12}

Figure 11  TRIR spectra of Zn\textsubscript{26} in PrCN observed following 560 nm excitation. Time delays are in ps and arrows indicate rise and decay of transients.\textsuperscript{12}
4.2 Abstract

The aim of this chapter is to investigate the efficiency of communication between a porphyrin and a metal carbonyl moiety across π substituents arranged in an orthogonal manner at the meso position of a porphyrin macrocycle. Photophysical measurements have been carried out on these systems and are discussed below.\textsuperscript{14} With respect to this study, an increased understanding of the initial photoprocesses that occur immediately after excitation of the monopyridyltriphenyl porphyrin metal pentacarbonyl complexes (M = W or Cr) was sought. TRIR spectroscopy with picosecond resolution should provide such information. **Pyridine-W(CO)\textsubscript{5}** was used as a model compound.

![Pyridine-W(CO)\textsubscript{5}](image)

**Figure 12** Porphyrin metal pentacarbonyl systems under investigation.
The porphyrin metal pentacarbonyl complexes were synthesised previously and examined by steady state fluorescence techniques and transient absorbance spectroscopy on a µs timebase. Only minor perturbations in the absorbance and luminescence properties of the porphyrins resulted from the presence of the metal carbonyl adducts when compared to the non-coordinated porphyrin.

Steady state photolysis of the complexes showed that sensitisation of the porphyrin ($\lambda_{exc} = 550$ nm) resulted in efficient cleavage of the metal pentacarbonyl moiety. In CO saturated solution, cleavage of the pyridine N – M bond (M = W or Cr) resulted in the formation of M(CO)$_6$ as was evidenced by a new absorbance band at ~ 290 nm. Even in Ar saturated solutions, cleavage of the N-M bond was observed. For the zinc porphyrins, spectral changes indicated cleavage of the pyridine N – M bond (M = W or Cr) was followed by coordination of zinc from one porphyrin with a pyridine of another and formation of a zinc porphyrin polymer. Since the pyridine-M(CO)$_5$ moiety (M = W or Cr) does not itself absorb above 480 nm, this would suggest that although the porphyrins retain their spectroscopic identity upon complexation, there is significant communication between the two molecular components.

Transient absorbance spectroscopy ($\lambda_{exc} = 532$ nm) on a µs timebase of ZnMPyTPP-M(CO)$_5$ showed population of the excited states associated with the metalloporphyrin unit and not the pyridine-M(CO)$_5$ moiety. The transient absorbance difference spectrum possessed spectral features similar to that of the triplet state of the uncomplexed metalloporphyrin, ZnTPP. The lifetimes of the triplet excited state were somewhat shorter for the metal carbonyl metalloporphyrin (~15 µs) compared to the uncoordinated metalloporphyrin (20 µs). Also measurements carried out using various concentrations of CO confirmed that the lifetime of the triplet state was unaffected. The sample underwent loss of M(CO)$_5$ during the experiments as formation of M(CO)$_6$ was confirmed by IR spectroscopy. Changes observed in the Q band region of the porphyrin complex were attributed to cleavage of the N – M bond (M = W or Cr) and subsequent formation of the zinc porphyrin polymer.
A comprehensive investigation into the primary photoprocesses that occur following excitation will be carried out using TRIR spectroscopy. The metal pentacarbonyl moieties act as excellent reporter groups for infrared vibrational spectroscopy. A wealth of publications on various substituted pyridine-\(\text{M(CO)}_5\) complexes exists which should aid in the identification of transient species and subsequent product formation. With the ability of picosecond techniques, time resolved studies of reaction dynamics on the time scale of solvent motion can be probed.

Time resolved infrared studies allowed the direct observation of photoactive states, formed following excitation, through shifts in metal carbonyl absorbance bands. The TRIR data enabled identification of key excited states which are populated following photolysis.
4.3 Experimental

4.3.1 Materials

All syntheses were carried out under an atmosphere of argon or nitrogen using standard Schlenk techniques unless otherwise stated. All solvents were supplied by the Aldrich Chemical Company. Dichloromethane, chloroform, diethyl ether, pentane and hexane were dried over MgSO$_4$ prior to use. Tetrahydrofuran (THF) was distilled from sodium metal using benzophenone and used immediately. All organic reagents were purchased from the Aldrich Chemical Company and used without further purification unless stated otherwise. Pyrrole was distilled over KOH under reduced pressure prior to use. The hexacarbonyls, W(CO)$_6$ and Cr(CO)$_6$ were used without further purification. All mobile phases for column chromatography were dried over MgSO$_4$ and silica gel (Merck) was used as received. All solvents used in TRIR experiments were of spectroscopic grade and used without further purification. All solvents were deoxygenated by purging with pure argon or nitrogen for ~10 minutes.

4.3.2 Equipment

NMR spectra were recorded on a Bruker model AC 400 MHz spectrometer and Bruker model ANC 600MHz spectrometer using CDCl$_3$ as solvent. All NMR spectra were calibrated according to the residual solvent peak, i.e. CHCl$_3$ at 7.26 ppm for all $^1$H spectra and 77.16 ppm for all $^{13}$C spectra. Chemical shifts ($\delta$) are given in parts per million (ppm). Proton coupling constants ($J$) are given in Hertz (Hz). All UV-vis spectra were measured on an Agilent Technologies 8453 photodiode array spectrometer using a 1 cm$^3$ quartz cell. IR spectra were recorded on a Perkin-Elmer 2000 FT-IR spectrophotometer (2 cm$^{-1}$ resolution) in a 0.1 mm sodium chloride liquid solution cell. Picosecond time resolved infra-red spectroscopy was carried out as described previously.$^{13}$

4.3.3 Synthesis

All porphyrins were synthesised as described$^{14}$ using an adapted method by Adler et al.$^{15}$ The pentacarbonyl complexes were synthesised using a method described by Stromeier.$^{16}$
4.3.3.1 5-(4-Pyridyl)-10,15,20-triphenyl porphyrin (MPyTPP)

The monopyridyltriphenyl porphyrin was prepared via a mixed aldehyde condensation reaction. Freshly distilled pyrrole (100 mmol, 7.0 ml), benzaldehyde (75 mmol, 8.0 ml) and 4-pyridine carboxaldehyde (25 mmol, 2.35 ml) were added to 99 % propionic acid (250 ml) and brought to reflux temperature. The acidic solution was allowed to reflux for 2 hrs and gradually turned black. The mixture was allowed to cool and placed in the fridge overnight. The black solution was filtered and the purple crystals formed were collected and washed several times with methanol to give a bright purple crystalline solid. This method typically gave a yield of 2 g of crude product.
Thin layer chromatography using chloroform : ethanol (98 : 2) as mobile phase indicated the presence of a mixture of six porphyrins formed during the reaction. The compounds formed were 5,10,15,20-tetraphenylporphyrin (H$_2$TPP), 5-(4-pyridyl)-10,15,20-triphenylporphyrin (MPyTPP), cis-5,10-(4-dipyridyl)-15,20-diphenylporphyrin (cis-DPyDPP), trans-5,15-(4-dipyridyl)-10,20-diphenylporphyrin (trans-DPyDPP), 5,10,15-(4-pyridyl)-20-phenylporphyrin (TPyMPP) and 5,10,15,20-tetra(4-pyridyl)porphyrin (TPyP).

The crude porphyrin mixture was purified on a silica gel column. The initial eluent was chloroform : ethanol (98 : 2) and this eluted the first fraction containing H$_2$TPP. Subsequent purifications by column chromatography used a mobile phase with increasing polarity (chloroform : ethanol (97 : 3) and chloroform : ethanol (96 : 4)) to separate the remaining porphyrins. Only MPyTPP was required for this study.

$^1$H NMR (400 MHz, CDCl$_3$): 9.04 (2H, d, $J = 8$ Hz), 8.89 (2H, d, $J = 4$ Hz), 8.86 (4H, s), 8.80 (2H, d, $J = 4$ Hz) 8.23 – 8.20 (6H, m), 8.18 (2H, d, $J = 8$ Hz) 7.81 – 7.73 (9H, m), -2.83 (2H, s) ppm. UV-vis (CH$_2$Cl$_2$): 418, 514, 548, 588, 644 nm.
4.3.3.2 Zinc(II) 5-(4-pyridyl)-10,15,20-triphenyl porphyrin (ZnMPyTPP)

ZnMPyTPP was synthesised via Lindsey’s method for the metallation of porphyrins. The freebase porphyrin, MPyTPP, (0.32 mmol, 200 mg) was dissolved in ca. 50 ml chloroform and the solution was purged with argon for 10 minutes. An excess of Zn(OAc)$_2$ (0.40 mmol, 73 mg) was first dissolved in ca. 5 ml MeOH and then added to the porphyrin solution. The reaction mixture was allowed to stir overnight at room temperature under a nitrogen atmosphere. All solvents were removed under reduced pressure leaving a purple solid. This solid was dissolved in CH$_2$Cl$_2$ and washed successively with 5 % aqueous NaHCO$_3$, followed by water. The organic layer was dried over MgSO$_4$ and the solvent removed under reduced pressure. The metalloporphyrin were purified by column chromatography using silica and neat chloroform as mobile phase. Yield: 130 mg, 0.19 mmol, 60 %.

![Zinc pyridyl porphyrin structure]

Zinc pyridyl porphyrins aggregate in non-coordinating solvents and are a darker blue colour compared to the purple colour of ZnTPP. The $^1$H NMR showed evidence of aggregation.

$^1$H NMR (400 MHz, CDCl$_3$): 8.87 – 8.82 (m, pyrrole), 8.23 – 8.15 (m, pyrrole), 8.15 – 8.09 (m, phenyl) 7.77 – 7.64 (m, phenyl), 4.61 – 4.59 (m, 3,5-pyridyl), 23.58 – 3.56 (m, 2,6-pyridyl) ppm. UV-vis (CH$_2$Cl$_2$): 418, 562, 604 nm.
4.3.3.3 Preparation of 5-(4-pyridyl)-10,15,20-triphenyl porphyrin metal pentacarbonyl complexes (M = Cr or W)

4.3.3.3.1 5-(4-Pyridyl)-10,15,20-triphenyl porphyrin chromium pentacarbonyl (MPyTPP-Cr(CO)₅)

Initially chromium hexacarbonyl (0.68 mmol, 150 mg) was photolysed in freshly distilled THF (150 ml) that had been degassed for 15 minutes with nitrogen. The solution was photolysed with a Hg lamp. The solution was continually purged with nitrogen and after about 40 minutes the solution had turned a strong orange colour. Completion of photolysis and the formation of Cr(CO)₅THF was determined by IR spectroscopy. Depletion of the hexacarbonyl peak at 1979 cm⁻¹ and formation of the new pentacarbonyl peaks (2072, 1936 and 1893 cm⁻¹) indicated completion of the reaction. Following this, 5-(4-pyridyl)-10,15,20-triphenylporphyrin (0.32 mmol, 200 mg) was added to Cr(CO)₅THF under an atmosphere of nitrogen and allowed to stir overnight in darkness under an inert
atmosphere. Removal of the THF was carried out under reduced pressure on the rotary evaporator. The complex was then dissolved in chloroform and purified on a silica gel column using chloroform : pentane (90 : 10) as mobile phase. Unreacted hexacarbonyl was eluted initially from the column with any further hexacarbonyl impurities removed by sublimation under reduced pressure. The complex was recrystallised from cold pentane affording purple crystals. Yield: 163 mg, 0.20 mmol, 63 %. Spectroscopic data were in good agreement with reported data.14

\[ ^1\text{H NMR} \ (400 \text{ MHz, CDCl}_3): \] 9.01 – 8.99 (2H, m), 8.94 – 8.92 (2H, m), 8.86 (4H, s), 8.81 – 8.77 (2H, m), 8.21 (6H, d, \( J = 8 \text{ Hz} \)), 8.10 (2H, d, \( J = 4\text{Hz} \)), 7.87-7.74 (9H, m), -2.83 (2H, s) ppm.

\[ \text{IR (CH}_2\text{Cl}_2): \nu(\text{CO}) 2068, 1935, 1898 \text{ cm}^{-1}. \]

\[ \text{UV-vis (CH}_2\text{Cl}_2): 420, 516, 552, 590, 646 \text{ nm}. \]
4.3.3.3.2 Zinc(II)5-(4-pyridyl)-10,15,20-triphenyl porphyrin chromium pentacarbonyl (ZnMPyTPP-Cr(CO)$_5$)

Synthesis of ZnMPyTPP-Cr(CO)$_5$ was carried out in the same manner. Chromium hexacarbonyl (0.45 mmol, 100 mg) and ZnMPyTPP (0.074 mmol, 50 mg) were used. The complex was purified on a silica gel column using chloroform : pentane (90 : 10) as mobile phase. Unreacted hexacarbonyl impurities were removed by sublimation under reduced pressure. The complex was recrystallised from cold pentane affording purple crystals. Yield: 34 mg, 0.039 mmol, 53 %. Spectroscopic data were in good agreement with reported data.$^{14}$

$^1$H NMR (400 MHz, CDCl$_3$): 9.03-9.01 (1H, m), 8.98 – 8.95 (4H, m), 8.89 – 8.86 (3H, m), 8.85 – 8.83 (2H, m), 8.24 – 8.21 (4H, m), 8.12 – 8.07 (4H, m), 7.81 – 7.48 (9H, m) ppm. IR (CH$_2$Cl$_2$): ν(CO) 2069, 1934, 1895 cm$^{-1}$. UV-vis (CH$_2$Cl$_2$): 422, 548, 588 nm.
4.3.3.3 5-(4-Pyridyl)-10,15,20-triphenyl porphyrin tungsten pentacarbonyl (MPyTPP-W(CO)₅)

Synthesis of MPyTPP-W(CO)₅ was carried out in the same manner. Tungsten hexacarbonyl (0.43 mmol, 150 mg) and freebase porphyrin, MPyTPP, (0.32 mmol, 200 mg) were used. Purification on a silica gel column using chloroform : pentane (90 : 10) followed by sublimation under reduced pressure yielded the porphyrin complex. The product was recrystallised from cold pentane affording brownish-purple crystals. Yield: 204 mg, 0.22 mmol, 68 %. Spectroscopic data were in good agreement with reported data.¹⁴

¹H NMR (400 MHz, CDCl₃): 8.91 (2H, d, J = 8 Hz), 8.86 (2H, d, J = 4 Hz), 8.79 (4H, s), 8.71 (2H, d, J = 4 Hz), 8.14 – 8.12 (6H, m), 8.02 (2H, m), 7.76 – 7.66 (9H, m), -2.83 (2H, s) ppm. IR (CH₂Cl₂): ν(CO) 2070, 1928, 1896 cm⁻¹. UV-vis (CH₂Cl₂): 422, 516, 552, 590, 646 nm.
4.3.3.4 Zinc(II) 5-(4-pyridyl)-10,15,20-triphenyl porphyrin tungsten pentacarbonyl (ZnMPyTPP-W(CO)$_5$)

\[
\begin{array}{c}
W(CO)_6 \xrightarrow{\text{hv}} \text{W(CO)}_5\text{THF} + \text{CO} \\
\text{dry THF} \\
\text{N}_2 \\
\text{N}_2 \\
\text{ZnMPyTPP}
\end{array}
\]

Synthesis of ZnMPyTPP-W(CO)$_5$ was carried out in the same manner. Tungsten hexacarbonyl (0.28 mmol, 100 mg) and the zinc porphyrin, ZnMPyTPP, (0.074 mmol, 50 mg) were used. Purification on a silica gel column using a mobile phase of chloroform : pentane (90 : 10) followed by sublimation at reduced pressure gave the porphyrin complex. Recrystallised from cold pentane afforded the product as pinkish-purple crystals. Yield: 33 mg, 0.033 mmol, 45 %. Spectroscopic data were in good agreement with reported data.$^{14}$

$^1$H NMR (400 MHz, CDCl$_3$): 9.02 – 8.97 (5H, m), 8.89 – 8.84 (3H, m), 8.85 – 8.83 (2H, m), 8.20 – 8.17 (4H, m) 8.10 – 8.05 (4H, m), 7.80 – 7.55 (9H, m) ppm. IR (CH$_2$Cl$_2$): $\nu$(CO) 2071, 1929, 1894 cm$^{-1}$. UV-vis (CH$_2$Cl$_2$): 420, 550, 590 nm.
4.4 Results
4.4.1 UV-vis absorbance studies

The UV-vis spectrum of pyridine-W(CO)$_5$ is displayed in figure 13. Similar to other pyridine-W(CO)$_5$ complexes it possesses a LF transition at 382 nm and a MLCT band at ca. 430 nm.$^{18}$

![UV-vis spectrum of pyridine-W(CO)$_5$ recorded in CH$_2$Cl$_2$.](image)

Figure 14 displays the UV-vis spectra of MPyTPP and ZnMPyTPP. The absorbance spectra have been reported previously.$^{19}$ The UV-vis spectrum of the uncomplexed freebase porphyrin, MPyTPP, is similar to that of H$_2$TPP. It displayed a Soret $\lambda_{\text{max}}$ at 418 with four Q bands in the range 514 – 644 nm (Table 3). The UV-vis spectrum of ZnMPyTPP is akin to that of ZnTPP with a Soret $\lambda_{\text{max}}$ observed at 418 nm and two Q bands at 562 and 604 nm (Table 3). Pyridine is known to coordinate to the metal centre of a metalloporphyrin. In this case the N atom of the pyridine unit coordinates to the Zn atom of another porphyrin, leading to formation of a polymer.$^{19}$
Figure 14  UV-vis spectra of MPyTPP (blue line) and ZnMPyTPP polymer (red line) recorded in CH$_2$Cl$_2$. Spectra have been normalised at their $\lambda_{\text{max}}$.

Following complexation of the monopyridyltriphenyl porphyrins with W(CO)$_5$ and Cr(CO)$_5$, the UV-vis spectra were still dominated by porphyrin transitions with only a slight shift in band position observed (Fig. 15). No tungsten or chromium based absorbances were detected for the porphyrin-W(CO)$_5$ and porphyrin-Cr(CO)$_5$ complexes. The electronic absorbance spectral features of the porphyrins synthesised in this study are listed in table 3.

The freebase pyridyl porphyrins complexed with metal pentacarbonyls, MPyTPP-W(CO)$_5$ and MPyTPP-Cr(CO)$_5$, possessed an intense Soret band and four Q bands, the Soret band red shifted by 2 and 4 nm respectively with a 2 nm red shift observed in all Q bands. No pyridine-M(CO)$_5$ transitions are observed in the porphyrin metal pentacarbonyl complexes. However these transitions may be masked by the intensity of the porphyrin Soret band ($\varepsilon = 40,000 - 80,000$ M$^{-1}$ cm$^{-1}$) compared to that of pyridine-M(CO)$_5$ ($\varepsilon = \sim 7,000$ M$^{-1}$ cm$^{-1}$). The small but consistent bathochromic shift of the Soret and Q bands indicates a weak electronic interaction between the metal centre and the porphyrin macrocycle.$^{20}$
Complexation of the zinc porphyrin with the metal pentacarbonyl moiety produced electronic absorbance spectra that were similar to that of the uncomplexed zinc porphyrins. However substantial blue shifts were observed in the Q band region of 14 – 16 nm (Table 3). The reason for this large shift in the Q bands (compared to the 2 nm red shift observed with freebase analogues) is that the environment of the meso pyridyl group was changed more dramatically. The N-Zn bond is intrinsically weak and a complexing ligand such as M(CO)$_5$ breaks the bond. The pyridine ligand of the metalloporphyrin was no longer coordinated to the zinc atom of an adjacent macrocycle but coordinated to the metal pentacarbonyl fragment. Again, the UV-vis spectra are dominated by porphyrin transitions and no pyridyl tungsten or pyridyl chromium based absorbances were detected in the porphyrin complexes. As the extinction coefficients of the porphyrin are higher than that of the free pyridine metal pentacarbonyl, it was expected that the tungsten (or chromium) based absorbance would be masked.

Figure 15  UV-vis spectra of MPyTPP-Cr(CO)$_5$ (blue line) and ZnMPyTPP-Cr(CO)$_5$ (red line) recorded in CH$_2$Cl$_2$. Spectra have been normalised at their $\lambda_{\text{max}}$.  

304
<table>
<thead>
<tr>
<th>Porphyrin</th>
<th>Soret $\lambda_{\text{max}}$ (nm)</th>
<th>Q bands (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MPyTPP</td>
<td>418</td>
<td>514, 548, 588, 644</td>
</tr>
<tr>
<td>ZnMPyTPP polymer</td>
<td>418</td>
<td>562, 604</td>
</tr>
<tr>
<td>MPyTPP-W(CO)$_5$</td>
<td>422</td>
<td>516, 552, 590, 646</td>
</tr>
<tr>
<td>ZnMPyTPP-W(CO)$_5$</td>
<td>420</td>
<td>548, 588</td>
</tr>
<tr>
<td>MPyTPP-Cr(CO)$_5$</td>
<td>420</td>
<td>516, 552, 590, 646</td>
</tr>
<tr>
<td>ZnMPyTPP-Cr(CO)$_5$</td>
<td>422</td>
<td>548, 588</td>
</tr>
</tbody>
</table>

*Table 3  Absorbance maxima of freebase and zinc(II) porphyrins and metal pentacarbonyl complexes.*
4.4.2 IR studies

The ground state IR spectrum of pyridine-W(CO)$_5$ was reported previously$^{18}$ and displays three IR active $\nu$(CO) vibrations at 2073, 1935 and 1921 cm$^{-1}$ (Fig. 16). Pyridine-W(CO)$_5$ possesses a $C_{4v}$ local symmetry and as such displays three IR-active $\nu$(CO) vibrations which correspond to $2A_1$ and $E$ stretching vibrations.$^{18}$ The infrared spectrum was dominated by the strong $E$ band. The weak $A_1^2$ band, attributed to in-phase stretching vibrations of the four cis CO ligands, occurred at higher frequency. The $A_1^1$ $\nu$(CO) vibration, involving mainly the trans CO ligand, was displayed on the lower energy side of the $E$ band.

![Figure 16](https://example.com/figure16.png)

*Figure 16  IR spectrum of pyridine-W(CO)$_5$ recorded in CH$_2$Cl$_2$.*

Complexation of tungsten pentacarbonyl and chromium pentacarbonyl with the pyridyl porphyrins resulted in IR spectra with three similar IR vibrations. The IR spectra of the freebase and zinc(II) pyridyl porphyrin chromium pentacarbonyl complexes is shown in figure 17.
The IR spectroscopic data (metal carbonyl region) for the freebase and zinc monopyridyltriphenyl porphyrin M(CO)$_5$ complexes are presented in Table 4. The ground state infrared spectra displayed three bands in the range 2072 - 1895 cm$^{-1}$. This was consistent with the local C$_{4v}$ symmetry of the pentacarbonyl moiety.$^{21}$ As observed for pyridine-W(CO)$_5$, the largest stretching vibration was the E band, a weak A$_{1g}$ band attributed to predominantly in-phase stretching vibrations of the four cis carbonyl ligands was at higher frequencies. The A$_{1u}$ v(CO) vibration, involving mainly the trans CO ligand, was manifested on the low-energy side of the E band.$^{22}$ According to Kolodziej et al.$^{23}$ the spectral data in figure 17 confirms that the metal atom is bound to the nitrogen atom in the porphyrin complex. No evidence of the dissubstituted tetracarbonyl complex due to coordination of two porphyrin moieties to the metal was observed. Variation of the solvent from THF to dichloromethane to acetonitrile had little effect on the carbonyl stretching frequencies (less than 2 cm$^{-1}$).
Table 4 Carbonyl stretching frequencies of pyridine and porphyrin metal pentacarbonyl complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>v(CO) (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyridine-W(CO)$_5$</td>
<td>2073, 1935, 1921</td>
</tr>
<tr>
<td>MPyTPP-W(CO)$_5$</td>
<td>2070, 1928, 1896</td>
</tr>
<tr>
<td>ZnMPyTPP-W(CO)$_5$</td>
<td>2071, 1930, 1894</td>
</tr>
<tr>
<td>MPyTPP-Cr(CO)$_5$</td>
<td>2068, 1935, 1898</td>
</tr>
<tr>
<td>ZnMPyTPP-Cr(CO)$_5$</td>
<td>2069, 1936, 1895</td>
</tr>
</tbody>
</table>
4.4.3 Picosecond time resolved infrared studies

A ps-TRIR investigation of pyridine-W(CO)$_5$, and monopyridyltriphenyl porphyrin metal pentacarbonyls (M = W or Cr) was performed. All of the TRIR studies reported herein were conducted in THF solution. Excitation was achieved using ~ 150 fs pulses of 400 and 532 nm radiation, and the resulting spectral changes were measured with picosecond time resolution in the 1800 – 2100 cm$^{-1}$ region.

The TRIR spectrum of pyridine-W(CO)$_5$ in THF was obtained following 400 nm excitation (Fig. 18). Within 1 ps of the excitation pulse the $\nu$(CO) bands of the parent complex at 2069, 1937 and 1924 cm$^{-1}$ were depleted (negative bands in the difference spectra) and new features were formed at 2074, 1960, 1928 and 1887 cm$^{-1}$. Over the subsequent 100 ps these IR stretching vibrations decayed with the appearance of new bands at 2074, 1937 and 1887 cm$^{-1}$, which remained on the nanosecond timescale. Reliable decay kinetics could not be obtained as the bleaches and transients overlapped each other.

![TRIR difference spectra in the delay range 3 – 1000 ps following excitation of pyridine-W(CO)$_5$ in THF following 400 nm excitation.](image)

**Figure 18** TRIR difference spectra in the delay range 3 – 1000 ps following excitation of pyridine-W(CO)$_5$ in THF following 400 nm excitation.
The TRIR spectra of MPyTPP-W(CO)$_5$ in THF was obtained following 400 nm excitation (Fig. 19). The spectral features were quite different to those previously observed for pyridine-W(CO)$_5$. Depletion of the parent bands at 2070, 1931 and 1989 cm$^{-1}$ occurred within the laser pulse. Simultaneously, three new bands were produced at 1912 and 1944 with a third band in the region 2075 - 2065 cm$^{-1}$. As the latter band overlapped with the bleach of the parent material (2070 cm$^{-1}$) the position of the band could not be accurately determined. Over the subsequent 100 ps these bands decayed with almost complete regeneration of the parent species. Very weak bands were present at 2070, 1935 and 1894 cm$^{-1}$ in the spectrum recorded at 1 ns.

**Figure 19**  TRIR difference spectra in the delay range 3 – 1000 ps following excitation of MPyTPP-W(CO)$_5$ in THF following 400 nm excitation.
The TRIR spectra of ZnMPyTPP-W(CO)$_5$ in THF were obtained following excitation at 400 nm (Fig. 20). Metallation of the porphyrin macrocycle with zinc appeared to have little effect on the processes observed in the $\nu$(CO) spectral range. Depletion of the parent carbonyl bands at 2071, 1930 and 1898 cm$^{-1}$ occurred within the laser pulse (1 ps) with concomitant generation of positive metal carbonyl bands at 1912 and 1944 cm$^{-1}$ with a third band in the range 2065 – 2075 cm$^{-1}$. The third band overlapped with the parent bleach and was at the edge of the observation window thus a reliable position for the band could not be obtained. These bands decayed over approximately 100 ps. Weak bands were observed in the 1 ns spectrum at 2071, 1940 and 1984 cm$^{-1}$ which indicated that a minor photoproduct was formed, albeit in very small quantities.

![Figure 20](image.png)

**Figure 20** TRIR difference spectra in the delay range 3 – 1000 ps following excitation of ZnMPyTPP-W(CO)$_5$ in THF following 400 nm excitation.
The TRIR spectrum of MPyTPP-Cr(CO)$_5$ in THF was obtained following excitation at 400 nm (Fig. 21). The excited state spectral profile acquired was similar to that of the tungsten system. Bleaching of the parent bands at 2069, 1934 and 1901 cm$^{-1}$ was observed within the laser pulse with product bands simultaneously generated at 1915, 1952 cm$^{-1}$ and a third in the region of the parent bleach 2064 – 2073 cm$^{-1}$. Decay of the transient species occurred over approximately 100 ps. However, the chromium system was not as reversible as the tungsten analogues and product bands were evident at 1968 and 1838 cm$^{-1}$ in the final spectrum (1 ns) with a further IR band possibly where the parent bleach occurs at 2069 cm$^{-1}$. (Note: the negative band at 2012 cm$^{-1}$ and corresponding positive band at 2017 cm$^{-1}$ were artefacts in the system as they were present in negative time delays.)

Figure 21  TRIR difference spectra in the delay range 3 – 1000 ps following excitation of MPyTPP-Cr(CO)$_5$ in THF following 400 nm excitation.
The TRIR spectrum of ZnMPyTPP-Cr(CO)$_5$ in THF was obtained by excitation at 400 nm (Fig. 22). As observed previously for the tungsten analogues, metallation of the porphyrin macrocycle with zinc caused little change in the ν(CO) spectroscopic region of the chromium pentacarbonyl complex. The TRIR spectra was characterised by negative bleaching of the ground state carbonyl stretches at 2066, 1935 and 1901 cm$^{-1}$, observed in the first delay taken after the laser pulse (1 ps). Positive bands were generated concomitantly at 1954 and 1916 cm$^{-1}$ and again the higher frequency band overlapped with the parent bleach in the region 2066 – 2076 cm$^{-1}$. The transient species decayed over approximately 100 ps with apparent recovery of the parent bleaches. However the system was not fully reversible and permanent product bands remained in the final spectrum (1 ns) at 1952, 1915 and 1873 cm$^{-1}$. (Note: the negative band at 2012 cm$^{-1}$ and corresponding positive band at 2017 cm$^{-1}$ were artefacts in the system as they were present in negative time delays.)

![Figure 22](image_url)  

**Figure 22** TRIR difference spectra in the delay range 3 – 1000 ps following excitation of ZnMPyTPP-Cr(CO)$_5$ in THF following 400 nm excitation.
The TRIR spectrum of MPyTPP-Cr(CO)$_5$ in THF was obtained following excitation at 532 nm (Fig. 23). The spectral features were quite different to those previously observed following excitation at 400 nm. Depletion of the parent bands at 2064, 1935 and 1890 cm$^{-1}$ was observed within the laser pulse (1 ps) with product bands simultaneously generated at 1952, 1917 and 1895 cm$^{-1}$. Over the subsequent 30 ps these IR bands decayed with the appearance of new IR bands at 1943, 1903 and 1890 cm$^{-1}$ which remained on the nanosecond timescale. (Note: The high frequency band at 2064 cm$^{-1}$ was excluded from the spectrum as it was at the very edge of the observation window and reliable information could not be obtained.)

![TRIR difference spectra](image)

**Figure 23** TRIR difference spectra in the delay range 3 – 1000 ps following excitation of MPyTPP-Cr(CO)$_5$ in THF following 532 nm excitation.
4.5 **Discussion**

4.5.1 **Picosecond time resolved infrared studies**

Transient visible absorbance spectroscopy is very well suited to study the porphyrin moiety of the complexes due to the strong excited state absorbance. However, the complexes in this study benefit from the inclusion of metal carbonyls which provide a spectroscopic handle in the infrared through CO-stretching frequencies. Accordingly, picosecond time resolved infrared spectroscopy is an ideal tool for probing excited states.

The photochemistry of M(CO)$_6$ (M = Cr, W or Mo) has been extensively studied and their photochemistry is well documented. Transient visible absorbance studies have shown that CO loss occurs in less than 300 fs and that a solvent molecule occupies the vacant CO position in less than 2 ps.\(^\text{24}\) Transient IR experiments probing the CO-stretching region of W(CO)$_6$ showed a bleach at 1983 cm$^{-1}$ following irradiation which corresponded to the depletion of the ground state species and generation of new bands at 1956 and 1928 cm$^{-1}$ assigned to the photoproduct, W(CO)$_5$(n-hexane).\(^\text{25}\) Previous experiments have shown that after CO loss from M(CO)$_6$ (M = Cr, W or Mo) the stable photoproduct is not the bare M(CO)$_5$ molecule but a hexa-coordinate species of the form M(CO)$_5$(solvent), where a solvent molecule is weakly bound at the sixth ligand and forms rapidly even in relatively inert solvents.\(^\text{26}\)
4.5.1.1 Pyridine-W(CO)$_5$

Time resolved infrared studies on picosecond timescale for pyridine-W(CO)$_5$ in THF revealed very interesting excited state dynamics. Depletion of the ground state metal carbonyl stretches together with the generation of new IR bands occurred within the laser pulse (initial spectrum taken after 1 ps time delay). The negative IR bands in figure 18 were attributed to cleavage of the pyridyl nitrogen – tungsten bond. Cleavage of the N – W bond has been observed previously and reported to occur on a femtosecond timescale.\(^{25}\)

To provide assignments for the new IR features observed it is necessary to consider all possible outcomes of the initial solvation. THF has two effective binding arrangements: a σ bond to one of the H atoms or a η$^1$ coordination to oxygen. Previous studies have shown that a coordinated alkyl group can be best described as a “token ligand” that interacts weakly with the metal centre.\(^{27}\) If a stronger interaction is possible, then rearrangement to the thermodynamically favoured product will occur. In these studies the bands observed at 2074, 1960, 1928 and 1887 cm$^{-1}$ correspond to an intermediate formed by a H bond between the tungsten and the THF as shown in scheme 1. This species then rearranges in less than 100 ps to form the more stable (CO)$_5$W-η$^1$(O)-THF photoproduct, with IR stretching vibrations at 2074, 1937 and 1887 cm$^{-1}$.

Migration of solvated metal pentacarbonyl species (Cr(CO)$_5$) on solvent molecules is detailed in the literature for solvents other than THF.\(^{28}\) For instance, in pentanol, where both hydroxyl and alkyl groups were available for coordination to the site vacated by the photoeliminated carbonyl ligand, migration was observed from the alkyl to hydroxyl end of the solvent. The most thermodynamically stable complex involved coordination of the hydroxyl end of the solvent molecule to the metal carbonyl. If the initial solvation produced intermediates where the alkyl group was coordinated to the metal, rearrangement or exchange with solvent molecules occurred to form the most stable complex.

The rearrangement observed here is analogous to that previously reported for group 6 metal carbonyls in 1-hexanol and 1-hexyne.\(^{27}\) In the case of 1-hexanol, rearrangement occurred until the metal fragment coordinated to the hydroxyl group of the alcohol (from initially the alkyne end). For Cr(CO)$_6$ in 1-hexanol the rearrangement from alkyl to
hydroxyl was 1.2 ns. In the case of 1-hexyne, rearrangement from the alkyl end to a \( \eta^2 \) interaction with the alkyne occurred in less than 70 ps. The differences observed for Cr(CO)\(_5\) in moving from 1-hexanol to 1-hexyne was attributed to viscosity differences in these two solvents. 1-Hexanol exhibits a viscosity of 6.00 cP, while 1-hexyne has a much lower viscosity of 0.34 cP.\(^{29}\) A more viscous solvent will result in a large rearrangement time since the local solvent motions are smaller.

In the case of the ps-TRIR studies presented here, the rearrangement from the alkyl to oxygen bonded metal centre occurred over a slightly longer timescale of 100 ps. This is not surprising since the viscosity of THF is 0.46 cP.\(^{29}\) The applicability of bulk solvent viscosity in such type of rearrangements is not without precedence. Thus the changes observed in the TRIR spectra of pyridine-W(CO)\(_5\) are assigned to cleavage of the nitrogen tungsten bond, followed by formation of a weak \( \sigma \) bond from the metal to a H of THF. This species then rearranges in less than 100 ps to form (CO)\(_5\)-\( \eta^1\)(O)-THF. Evidence for the latter species was observed on the nanosecond timescale, and the bands observed at 2074, 1937 and 1887 cm\(^{-1}\) compare well to those reported for (CO)\(_5\)-\( \eta^1\)(O)-THF.

\[ \ce{[Diagram]} \]

*Scheme 1*  
Photoreaction following excitation at 400 nm of pyridine-W(CO)\(_5\) in THF.
4.5.1.2 Monopyridyltriphenylporphyrin-W(CO)$_5$ complexes

The photochemistry of MPyTPP-W(CO)$_5$ was quite different from that of pyridine-W(CO)$_5$. Depletion of the parent bands occurred within the laser pulse together with the generation of positive bands (Table 5). The negative bands in the TRIR spectra are due to a depletion of the ground state while the positive bands are assigned to an excited state species. This excited state species decays in less than 100 ps, with almost complete regeneration of the parent complex. Weak bands were evident at ~2071, 1935 and 1984 cm$^{-1}$ in the spectrum recorded after 1 ns. These bands compare well with those for W(CO)$_5$(THF), and are therefore attributed to minor quantities of this photoproduct.

Photolysis of the zinc porphyrin, ZnMPyTPP-W(CO)$_5$, resulted in excited state dynamics that were similar to that described for the freebase analogue. Depletion of the parent IR bands together with the generation of new bands occurred within the laser pulse (1 ps) (Table 5). The new bands are assigned to an excited state transient species that decays in less than 100 ps. Minor bands were observed at 1940 and 1984 cm$^{-1}$ are attributed to W(CO)$_5$(THF), *albeit*, in small quantities.

<table>
<thead>
<tr>
<th>Complex</th>
<th>v(CO) (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MPyTPP-W(CO)$_5$</td>
<td>~2070, 1931, 1898</td>
</tr>
<tr>
<td>MPyTPP-W(CO)$_5^*$ initial</td>
<td>~2075, 1944, 1912</td>
</tr>
<tr>
<td>MPyTPP-W(CO)$_5$ final</td>
<td>~2070, 1935, 1894</td>
</tr>
<tr>
<td>ZnMPyTPP-W(CO)$_5$</td>
<td>~2071, 1930, 1898</td>
</tr>
<tr>
<td>ZnMPyTPP-W(CO)$_5^*$ initial</td>
<td>~2075, 1944, 1912</td>
</tr>
<tr>
<td>ZnMPyTPP-W(CO)$_5$ final</td>
<td>~2073, 1940, 1984</td>
</tr>
<tr>
<td>W(CO)$_5$(THF)</td>
<td>2075, 1930, 1890</td>
</tr>
</tbody>
</table>

*Table 5* Frequencies (cm$^{-1}$) in the v(CO) region of species involved in photochemistry of porphyrin pyridyl tungsten pentacarbonyl.
The transient species generated for both the freebase and zinc pyridyl porphyrin tungsten pentacarbonyl were attributed to a porphyrin excited state which was formed on a picosecond timescale. Relaxation of the porphyrin excited state results in regeneration of most of the parent complex, as observed by recovery of the parent bleaches and decay of the transient species, indicating that the pyridyl porphyrin tungsten pentacarbonyl system underwent a process that was almost fully reversible. However, minor amounts of cleavage of the nitrogen – tungsten bond occurred as was evidenced by the small residual peaks at ~ 2070, 1935 and 1894 cm\(^{-1}\) due to the formation of W(CO)\(_5\)(THF).

Cleavage of the N-W bond is not very efficient following excitation at 400 nm, for the monopyridyltriphenyl porphyrin W(CO)\(_5\) complexes studied which contrasts with quantum yields reported for pyridine-W(CO)\(_5\). Wrighton et al. studied the photosubstitution reactivity of a series of substituted pyridine tungsten pentacarbonyl complexes.\(^{18a}\) Photosubstitution of both the pyridine and CO were observed, but the dominant reaction is efficient dissociation of the pyridine moiety following irradiation is into its lowest LF absorbance band. Quantum yields in the range 0.62 – 0.82 have been reported for various pyridine-W(CO)\(_5\) complexes following 436 nm excitation.\(^{18}\)
4.5.1.3 Monopyridyltriphenylporphyrin-Cr(CO)$_5$ complexes

The CO-stretch frequencies of the pyridyl porphyrin chromium pentacarbonyl complexes and transient species generated following photolysis (Table 6) were slightly shifted to higher energy when compared to those observed for the tungsten species which is consistent with previously observed systems.$^{25}$ Both the freebase and zinc analogues, MPyTPP-Cr(CO)$_5$ and ZnMPyTPP-Cr(CO)$_5$, underwent a similar process to the tungsten porphyrins following 400 nm excitation. Excitation of the freebase derivative MPyTPP-Cr(CO)$_5$ resulted in bleaching of the parent bands with generation of an excited state transient species within the laser pulse. These IR bands decayed over approximately 100 ps, to regenerate the parent complex. The chromium system does not appear to be as photoreversible as the tungsten systems, as it is obvious from the final spectrum (1 ns) that the parent bands do not recover. Also the intensity of the bands assigned to Cr(CO)$_5$THF at ~2071, 1938 and 1968 cm$^{-1}$, present in the final spectrum recorded after 1 ns are greater than those observed for the tungsten analogues. A higher quantum yield for photoprocesses involving chromium carbonyl systems is not without precedence in the literature.$^{30}$ A comparable sequence of events was observed for ZnMPyTPP-Cr(CO)$_5$ following 400 nm excitation.

<table>
<thead>
<tr>
<th>Complex</th>
<th>ν(CO) (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MPyTPP-Cr(CO)$_5$</td>
<td>2069, 1934, 1901</td>
</tr>
<tr>
<td>MPyTPP-Cr(CO)$_5^*$ initial</td>
<td>~2072, 1952, 1915</td>
</tr>
<tr>
<td>MPyTPP-Cr(CO)$_5$ final</td>
<td>~2072, 1938, 1968</td>
</tr>
<tr>
<td>ZnMPyTPP-Cr(CO)$_5$</td>
<td>~2066, 1935, 1901</td>
</tr>
<tr>
<td>ZnMPyTPP-Cr(CO)$_5^*$ initial</td>
<td>~2074, 1954, 1916</td>
</tr>
<tr>
<td>ZnMPyTPP-Cr(CO)$_5$ final</td>
<td>~2072, 1949, 1873</td>
</tr>
<tr>
<td>Cr(CO)$_5$(THF)</td>
<td>2071, 1938, 1895</td>
</tr>
</tbody>
</table>

Table 6 Frequencies (cm$^{-1}$) in the ν(CO) region of species involved in photochemistry of porphyrin pyridyl tungsten pentacarbonyl.
In addition to studies at 400 nm, the freebase pyridyl porphyrin chromium pentacarbonyl was also studied at 532 nm. The spectral characteristics following 532 nm excitation were significantly different to those observed following 400 nm excitation. They were in fact similar to the spectral characteristics observed for pyridine-W(CO)$_5$ as opposed to the porphyrin metal pentacarbonyl systems. Following excitation of MPyTPP-Cr(CO)$_5$ at 532 nm, depletion of the ground state metal carbonyl stretch occurred within the laser pulse (1 ps) together with the generation of positive transient bands. These bands decay in 30 ps with the generation of positive bands that remained on a nanosecond timescale. In this study, the parent band does not recover indicating efficient photocleavage of the pyridyl nitrogen – chromium bond occurred. The initial bands observed correspond to the intermediate formed by a H bond between the chromium pentacarbonyl and the solvent, THF. This species rearranges to form the more stable (CO)$_5$Cr-η$^1$(O)THF photoproduct, with new IR stretching bands growing in after 30 ps. However due to overlap of the parent bleach and stretching vibrations of the photoproduct accurate band positions for the (CO)$_5$Cr-η$^1$(O)THF photoproduct is difficult to determine. Excitation at 532 nm, where absorbance by the porphyrin moiety occurs preferentially, caused efficient photocleavage of the nitrogen – chromium bond and thus photoejection of the chromium pentacarbonyl species within 1 ps. Therefore communication between the porphyrin moiety and the metal centre must be very efficient at 532 nm.

However it is unexpected that photophysical process would be different following 400 nm excitation compared to 532 nm excitation. This is because excitation at $\lambda_{\text{exc}} = 400$ nm populates the $S_2$ state of the porphyrin, which would be expected to lead to efficient population of the $S_1$ state via rapid internal conversion. Since the $S_1$ state is populated directly by 532 nm excitation similar behaviour would be expected at both excitation wavelengths.
For the uncomplexed freebase porphyrin, \textbf{MPyTPP}, excitation at $\lambda_{\text{exc}} = 532$ nm resulted in formation of the $S_1$ singlet excited state with a lifetime of 10 ns followed by population of the triplet excited state \textit{via} intersystem crossing. The triplet lifetime was measured to be 30 $\mu$s. A representation of the processes is shown below (Fig. 24).

\textit{Figure 24} \hspace{1cm} \textit{Energy level diagram depicting the photoprocesses in MPyTPP following 532 nm excitation.}
Excitation of $\text{MPyTPP-M(CO)}_5$ ($M = \text{W or Cr}$) at $\lambda_{\text{exc}} = 400 \text{ nm}$ (Soret band) results in population of the $S_2$ state of the porphyrin (Fig. 25). Rapid internal conversion leads to population of the $S_1$ excited state. Intersystem crossing then occurs leading to the triplet excited state followed by relaxation to the ground state. Cleavage of the pyridyl N – M bond ($M = \text{W or Cr}$) does not occur.

Figure 25  
Energy level diagram depicting the photoprocesses in $\text{MPyTPP-M(CO)}_5$ $M = (\text{W or Cr})$ following 400 nm excitation.
Excitation of MPyTPP-Cr(CO)$_5$ at $\lambda_{exc} = 532$ nm (Q band region) results in formation of the first singlet excited state, the lifetime of which was reported as 6 ns, shorter than that of the uncomplexed porphyrin, MPyTPP. Efficient cleavage of the pyridyl nitrogen - chromium bond takes place on a picosecond timescale leading to formation of Cr(CO)$_5$(THF) which rearranges in the solvent to the most thermodynamically stable form over 30 ps. The uncomplexed porphyrin in its triplet state, was previously observed following cleavage and possessed a lifetime of 27 $\mu$s (Fig. 26).

![Energy level diagram depicting the photoproceses in MPyTPP-Cr(CO)$_5$ following 532 nm excitation.](image)

**Figure 26**  
*Energy level diagram depicting the photoprocesses in MPyTPP-Cr(CO)$_5$ following 532 nm excitation.*

Clearly another process occurs following 400 nm excitation that can explain the discrepancy observed in the TRIR data and discussed above. Further investigative work on these systems is therefore required.
A plausible schematic representation of the observed photochemistry is depicted below. Excitation at $\lambda_{\text{exc}} = 532$ nm, causes population of the singlet state of MPyTPP-Cr(CO)$_5$. Loss of the M(CO)$_5$ moiety occurs from this excited state in less than 1 ps. Subsequent intersystem crossing leads to population of the excited triplet state of the uncomplexed porphyrin where relaxation to the ground state occurs. The M(CO)$_5$ moiety is efficiently scavenged by the solvent and forms the Cr(CO)$_5$(THF) adduct.

Scheme 2  Plausible schematic diagram of photoprocesses occurring following 532 nm excitation.
4.6 Conclusion

Picosecond TRIR studies were carried out on pyridine-W(CO)$_5$ and a range of pyridyl porphyrin metal pentacarbonyl complexes in THF, which allowed for the identification of intermediate species following photolysis. Excitation of pyridine-W(CO)$_5$ at 400 nm resulted in photodissociation of the metal pentacarbonyl moiety with subsequent coordination to a solvent molecule within 1 ps. Over 100 ps, rearrangement of the initially formed σ H bond between the tungsten pentacarbonyl and THF to the more stable (CO)$_5$Cr-η$^1$(O)THF photoproduct occurred. This is the first report detailing the rearrangement of metal pentacarbonyl species in THF solution.

Excitation of all porphyrin complexes at 400 nm resulted in formation of a porphyrin based excited state that decayed in less than 100 ps to regenerate the parent porphyrin complexes. As TRIR only provides information about the carbonyl moiety, little information can be garnered from this. There is a radial redistribution of electron density in the porphyrin macrocycle which results in less electron density on the metal (M = W or Cr). This results in less backbonding on the carbonyl ligands thus the observed IR bands of the transient species were at higher energy. For both tungsten and chromium analogues evidence for both (THF)Cr(CO)$_5$ and (THF)W(CO)$_5$, were present in the final spectra (1 ns), although the IR bands were weak.

However excitation of MPyTPP-Cr(CO)$_5$ at 532 nm resulted in photodissociation of the metal pentacarbonyl moiety, with subsequent coordination to a solvent molecule within 1 ps, and rearrangement of the initially formed σ H bond between the chromium pentacarbonyl and the THF to the more stable (CO)$_5$Cr-η$^1$(O)THF photoproduct. This is the first report detailing the rearrangement of metal pentacarbonyl species in THF solution.
4.7 Bibliography


Chapter 5

The synthesis and photophysical properties of a series of dipyrromethanes, a related borondifluoride dipyrrin and bis(dipyrrinato)zinc(II) complex.

Chapter five commences with a short literature review on the synthesis and photophysics of dipyrromethanes and dipyrrin compounds. The synthesis of a series of substituted thienyl dipyrromethanes, related dipyrrin complexes and corresponding dicobalt complexes is presented. Preliminary photophysical measurements are also discussed.
5.1 Literature Survey

5.1.1 Dipyrrromethanes

Polypyrrolic compounds are of wide interest in various fields of research from porphyrin chemistry\textsuperscript{1} to medicine.\textsuperscript{2} Dipyrrromethanes occupy a central place in these areas as they are building blocks for many of the architectures involved. Similar to porphyrins, the bi-pyrrolic molecules can bear substituents at the $\beta$ or meso positions. In the past a great number of step wise procedures have been published detailing the synthesis of both $\beta$ substituted and meso substituted dipyrrromethanes. The first synthetic dipyrrromethanes were $\beta$ substituted which were produced during the late 1960’s under very harsh conditions.\textsuperscript{3} Subsequent procedures focused on meso substituted derivatives and involved the self-condensation of an appropriate pyrrole carbinol cation precursor under acidic conditions using Montmorillonite clay\textsuperscript{4} or $p$-toluenesulphonic acid.\textsuperscript{5} One-flask condensations of pyrrole and the desired aldehyde in various acidified organic solvents were also reported.\textsuperscript{6} Workup generally involved several steps including column chromatography. Hammel et al. reported purification by flash chromatography followed by Kügelrohr distillation.\textsuperscript{7}

Since then, Lindsey et al. developed the synthesis of meso aryl substituted dipyrrromethanes via a more accessible route.\textsuperscript{8} Their one flask synthetic method involved the room temperature reaction of an aldehyde with excess pyrrole. The appropriate aldehyde was dissolved in a 40 fold excess of pyrrole in the absence of solvent and the reaction was catalysed by an acid, e.g. trifluoroacetic acid or BF$_3$.OEt$_2$. This method afforded nine meso substituted dipyrrromethanes bearing different functional groups (Fig. 1).
However purification of the product by column chromatography restricted application of the synthetic method to small scale production (< 1 g batches). Examination of the crude reaction mixture revealed three principal reaction products: (1a) dipyrrmethane, (1b) α,β-linked “N-confused” dipyrrmethane and (1c) tripyrrane (Fig. 2). An extensive GC-MS investigation into the reaction parameters was undertaken using *meso* phenyl dipyrrmethane (1a) to establish what factors affected product composition. Initially it was noted that the rate of the reaction was rapid. Total consumption of the aldehyde was observed 5 minutes after addition of the acid catalyst. The concentration of acid catalyst was examined: increased concentration (0.316 equiv.) resulted in decreased production of
1c, reduced concentration (0.031 equiv.) caused a small increase in 1b and 1c production. Thus a 0.1 equivalent was selected as an optimal acid concentration. Also, TFA catalysis gave significantly lower amounts of 1b and 1c compared to BF$_3$OEt$_2$. The pyrrole : aldehyde ratio was examined from 5 : 1 to 80 : 1 and indicated that changing the ratio resulted in a change in product distribution: the higher the ratio the higher the yield of dipyrromethane, consistent with the hypothesis that a high pyrrole : aldehyde ratio prevents polymerisation. Purification by bulb-to-bulb distillation followed by recrystallisation resulted in analytically pure dipyrromethanes.

![Chemical structures](image)

**Figure 2 Products following acid catalysed condensation of benzaldehyde in excess pyrrole.**

However, dipyrromethanes derived from aldehydes bearing sensitive or large substituents could not be distilled and in such cases column chromatography was again employed for purification. Thus further refinement of the solventless synthesis of 1 (Fig. 1) was reported. Altering the pyrrole : aldehyde ratio (25 : 1 to 400 : 1) changed the product composition and reaction rate. Increasing excess pyrrole decreased reaction rate as the acid concentration was reduced. Although increasing the concentration of acid caused no significant change in product distribution. Darkening of the reaction mixture had been observed previously and the darkening was attributed to formation of oligomeric by-products that could not be identified. A series of Brønsted and Lewis acid catalysts were investigated. The ideal acid should give negligible unreacted aldehyde, a high yield of dipyrromethane and no darkening of reaction medium. Brønsted acids produced a substantial amount of tripyrrane and darkened reaction mixtures. Lewis acids gave good yield of the desired product with little darkening. InCl$_3$ and MgBr$_2$ produced the best
results of both product distribution and relative absence of darkening of the reaction mixture. Comparison of InCl$_3$ with TFA, revealed TFA catalysed condensations were faster and gave complete consumption of the aldehyde within 30 minutes. Although another distinction was observed, TFA catalysis gave a dark brown crude product which required further treatment with charcoal in hot ethanol in addition to the designed workup. The four step workup devised included: (1) quenching – using excess powdered NaOH, (2) filtering – recovered acid catalyst and base, (3) removal of excess pyrrole – repeated distillation enabled recovery of excess pyrrole, and (4) recrystallisation – afforded dipyrrromethane 1 (Fig. 1) as white crystals with yields greater than 50%.

An efficient one-step synthesis of dipyrrromethanes in water was later reported.$^{11}$ The dropwise addition of pyrrole to an aqueous solution (90 °C) of aldehyde in the presence of HCl, followed by 30-45 minutes stirring under an inert atmosphere, gave the corresponding dipyrrromethane in high yields. The dipyrrromethane was released from the aqueous layer as the reaction proceeded thus forcing the reaction to completion and protecting the product from further reactions. GC-MS indicated that exclusive formation of the dipyrrromethane in the first 30 minutes at 90 °C for all reactions. Only after 3 hours refluxing were the N-confused dipyrrromethane and tripyrrane detected. This low production of secondary products along with high yields and the non-toxic environmentally friendly solvent make this method quite advantageous.

Cation exchange resins have been used to produce meso substituted dipyrrromethanes.$^{12}$ The resins acted as heterogeneous solid acid catalysts that consist of a styrene divinylbenzene co-polymer matrix with sulphonic acid groups and each resin particle can be viewed as a mini reactor. Cation exchange resin was added to a solution of the substituted aromatic aldehyde and neat excess pyrrole which subsequently afforded the corresponding dipyrrromethanes that were readily crystallised in high yields (70 – 80 %). The mechanism of ion exchanger catalysed reactions in a non aqueous media is similar to that operating for usual heterogeneous catalysts – adsorption, surface reaction, desorption. The use of the macroporous cation exchange resin resulted in high selectivity and purity of product due to trace side reactions.
A photochemical synthesis of dipyrromethanes was reported by D’Auria et al. In this procedure, a mixture of pyrrole and aldehyde (694 : 1) was photolysed with a 125 W high pressure Hg arc lamp surrounded by a Pyrex water jacket for 3 hours. Reported yields for phenyldipyrromethane (1, Fig. 1) and thien-2-ylidipyrromethane (10, Scheme 1) were 50 and 59 % respectively. However Lindsey et al. questioned the validity of the photochemical reaction on a number of conditions. Illumination by a high pressure mercury lamp produces a significant amount of heat and the experimental information given by D’Auria et al. was deemed insufficient to assess the radiation absorbed by the reaction mixture as well as the reaction temperature. Lindsey and co-workers carried out thermal condensations of pyrrole and benzaldehyde. Stirring the mixture in the dark at 22 ºC for 24 hours in the absence of acid catalyst produced phenyldipyrromethane in 3 % yield. At 40 ºC, yields akin to the deliberately acid catalysed reaction were obtained (56 % after distillation). Reaction at 90 ºC was complete within 90 minutes with 42% isolated yield.

Since the formation of dipyrromethane has been shown to occur thermally, formation of the dipyrromethanes by purely photochemical processes has yet to be proven.

Meso thien-2-yl and thien-3-yl dipyrromethane were produced via a modification of Lindsey’s TFA catalysed condensation from the respective thiophenecarboxaldehyde and excess pyrrole (Scheme 1). Incorporation of a heterocycle (thiophene) in place of the usual arene group at the meso position retains the Cs symmetry of the molecule and imparts a third donor atom for metal binding. The geometry of the thiophene group in thien-2-yl dipyrromethane was suitable to participate in tripodal [NNS] type metal chelation, whereas the geometry of the thien-3-yl analogue does not allow such binding. Crystal structures of both dipyrromethanes were obtained. The X-ray structures confirm methane angles of ca. 111 – 112 ° defining pyramidalisation of the meso carbon.
Scheme 1  Synthesis of thienyl dipyrromethanes.
5.1.2 Dipyrrins

Dipyrrins are formally composed of a pyrrole ring and an azafulvene attached to each other through the $\alpha$ position.\(^{15}\) The acid catalysed condensation of 2-formyl pyrrole with a pyrrole unsubstituted at the 2' position produces *meso* unsubstituted dipyrrin (Rxn. 1).

\[
\begin{align*}
\text{R} = \text{alkyl substituent}
\end{align*}
\]

**Rxn. 1** *Synthesis of* **meso** unsubstituted dipyrrin, **12**, *by acid catalysed condensation*.

*Mesol* substituted dipyrrromethanes can be oxidised to yield dipyrrins that are often stable in their freebase form. Oxidation of dipyrrromethanes can be accomplished with a number of reagents, the most popular of which are 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and $p$-chloranil. Limitations occur when the *meso* substituent is an alkyl group or the dipyrrromethane is *meso* unsubstituted. In these cases consumption of the starting material without yielding the appropriate product is observed. The NMR spectra of freebase *meso* substituted dipyrrins demonstrate rapid tautomerisation. The signal arising from the proton bonded to the nitrogen is not always apparent and is generally attributed to hydrogen bonding with the solvent.

Although freebase *meso* aryl dipyrrins can be isolated, by column chromatography and/or recrystallisation, in most cases they are reacted *in situ* with a metal salt to form homoleptic *meso* aryl(dipyrrinato)metal complexes or with boron trifluoride diethyletherate to form borondifluoride dipyrrins.
In general, following deprotonation, the monoanionic dipyrrinato ligands form neutral homoleptic complexes. Dipyrrins have the propensity to form stable complexes with variety of metal ions resulting in bis (dipyrrinato) metal (II) or tris (dipyrrinato) metal (III) complexes, which are ideal for utilisation in supramolecular coordination chemistry. There have been numerous reports on dipyrrinato complexes with a wide variety of metals including, but not limited to Ni(II), Cu(II), and Zn(II). Historically, dipyrrins typically contained a full complement of α and β substituents around the chromophores. Though in recent years there has been an increase in publications on αβ-unsubstituted dipyrrinato complexes.

Dehydrogenation of meso phenyl dipyrromethane (1, Fig. 1) with DDQ and subsequent reaction with copper(II), nickel(II) and zinc(II) yielded the corresponding highly coloured metal chelates (Scheme 2). The UV-vis properties of the metal chelates were strongly dependent on the central metal. Nickel chelates (Ni-13 and Ni-14, Scheme 2) possessed very similar absorbance spectra. The phenyl moiety was approximately perpendicular to the plane of the dipyrrin, consequently it was not in full conjugation with the pyrrolic system and substituents on the phenyl group had minimal influence on the π system. The UV-vis spectrum of the zinc chelate (Zn-14, Scheme 2) was similar to that of the protonated ligand, with a λmax at 486 nm and less intense transitions in the region 320 – 350 nm, which indicated the absence of any metal-metal interactions. The λmax band was assigned to intraligand π-π* transitions and the bands at higher energy were attributed to charge transfer transitions. The nickel and copper chelates, (Ni-13 and Cu-14, Scheme 2), possessed the same spectral pattern with λmax at 474 nm and 484 nm respectively. These absorbance properties were similar to related α alkyl substituted metal chelates but hypsochromically shifted. The stereochemistry of the ligands around the central metal was strongly dependant on the metal type. Crystal structure analysis of Ni-13 revealed the molecule had D2 symmetry, with two equivalent dipyrrin ligands. This endowed a C2-axis passing through the p-hydrogens of the meso substituent, the methine carbons and the central metal. The N-Ni-N bond angle was 152.5 ° and all four Ni-N distances were equal (1.879 Å). Both the nickel and copper bis(dipyrrinato)complexes (Ni-13, Ni-14, Cu-14) were assigned distorted square planar geometry while the zinc complex (Zn-14) was assigned a tetrahedral geometry.
Scheme 2  
**Synthesis of dipyrrins and bis(dipyrrinato)complexes from dipyromethanes.**

Several methods were examined for the preparation of the dipyromethane precursors fused with a variety of phenylacetylene building blocks. Subsequent metallation of the freebase dipyromethanes resulted in formation of the target (dipyrrinato)copper(II) complexes (Cu15 - Cu18, Fig. 3). The complex, Cu15, was examined by X-ray crystallography. It displayed a four coordinate distorted square planar coordination geometry. The four Cu-N bond lengths were in the range 1.942 – 1.951 Å. The phenylacetylene arms lay out of the plane of the dipyrrin chelating groups and were essentially linear for both ligands attached to the copper centre. The combination of dipyrrin chelators with phenylacetylene groups provided rich absorbance chemistry. Precursor dipyromethanes of 15 and 16 displayed a $\lambda_{max}$ at 298 and 302 nm respectively, attributed to $\pi-\pi^*$ transitions of the phenylacetylene. A new absorbance band centred at 435 nm was observed for all dipyrrins following oxidation with DDQ, which was attributed to the $\pi-\pi^*$ transition of the dipyrrin aromatic system. Additional absorbances at higher energy (330 – 345 nm) were observed for the uncoordinated *para* substituted phenylacetylene dipyrrins (R = 15 and 17) that were not seen for uncoordinated *meta* substituted systems (R = 16 and 18), indicating that *meta* substitution on the central benzene ring disrupted the extended conjugation of the $\pi$ system. In complexes Cu15 –
Cu18 the high energy transition became more defined and shifted bathochromically (350 – 355 nm), and the authors tentatively assigned the absorbance band to π-π* charge transfer processes between the π system of the dipyrrin groups and the π system of the phenylacetylene moiety. In the absorbance spectra of Cu15 – Cu18, the feature associated solely with the dipyrrin π-π* transitions (λ_{max} = 435 nm) was lost in favour of two new transitions centred at 468 and 500 nm, the intensities of which differed significantly (ε = 61,700 vs. 32,600 M\(^{-1}\) cm\(^{-1}\)), that were consistent with similar compounds reported previously.\(^{19,21}\) The fluorescence spectra were obtained and notably only the para substituted dipyrromethanes (15 and 17) exhibited significant fluorescence with emission maxima at 352, 368 and ~460 nm. The two higher energy emission bands were ascribed to fluorescence from the extended phenylacetylene moiety. All oxidation products, dipyrrins and bis(dipyrrinato)copper(II) complexes were found to be virtually non-fluorescent.
En route to producing self assembling triads composed of two porphyrins and an intervening bis(dipyrrinato)metal complex, the synthesis and spectroscopic properties of bis(dipyrrinato)metal(II) complexes was described (19, Fig. 5). The facile formation of the complexes via a one flask synthesis involved oxidation of freebase dipyrrromethane with DDQ in the presence of metal acetates, resulted in bis(meso-phenyl-dipyrrinato)metal(II) complexes (19, M = Cu, Pd, and Zn). There was a striking difference in the absorbance spectra of freebase dipyrrins and their bis(dipyrrinato) metal(II) complexes, a change in the broad-band absorbance of the former to the more intense sharp features of the metallo complexes was observed. The absorbance and emission spectra of bis(mesophenylidipyrrinato)zinc(II), Zn19 are shown in figure 4. The absorbance band
centred at 485 nm arose from an $S_0 \rightarrow S_1$ excited state transition.\textsuperscript{16} The fluorescence spectrum possessed approximate mirror symmetry to the absorbance spectrum, with a Stokes shift of $\sim$660 cm$^{-1}$, although the vibronic overtone feature was less prominent in the emission. The fluorescence quantum yield was 0.007 in toluene and 0.002 in benzonitrile. Time resolved absorbance spectroscopy was carried out. In toluene $\text{Zn19}$ displayed multicomponent excited-state profiles. A fast phase ($ca.$ 9 ps) was attributed to vibrational cooling in the excited state manifold while a slower component ($ca.$ 93 ps) reflected population decay from $\text{Zn19}^*$. The latter phase was accompanied by substantial ground state recovery, indicative of little formation of longer lived transients such as a triplet excited state. In benzonitrile, the dynamics were different although the authors did state some uncertainty in the assignments. A fast phase ($ca.$ 6.5 ps) associated with $\text{Zn19}^*$ was followed by a slower decay phase ($\sim$1 ns) that may have developed from another excited state (e.g. charge transfer), followed by a substantial contribution ($ca.$ 30 \%) to a longer lived state ($> 5$ ns).

An ensuing study revealed that minor modifications of the meso substituents in bis(dipyrrinato)zinc(II) complexes transformed the molecules from very weak emitters that deactivated within 100 ps of photoexcitation to highly fluorescent chromophores with multi-nanosecond singlet excited state lifetimes.\textsuperscript{23} Replacement of phenyl with $p$-tert-
butylphenyl or mesityl groups ($\text{Zn19, Zn20, Zn21}$ respectively, Fig. 5), constrained aryl ring rotation. Only minor changes were observed in the absorbance characteristics of $\text{Zn19, Zn20}$ and $\text{Zn21}$, with intense absorbance bands ($\varepsilon = 115,000 \text{M}^{-1} \text{cm}^{-1}$) in the range 482 – 487 nm. Fluorescence spectra of $\text{Zn19, Zn20}$ and $\text{Zn21}$ were approximately mirror images of the absorbance spectra with a Stokes shift of 660, 580 and 940 cm$^{-1}$ respectively. Notably the Stokes shift of $\text{Zn20}$ was reduced compared to $\text{Zn19}$ (and $\text{Zn21}$), which reflected less conformational freedom in the ground and/or excited states, due to steric hindrance. Complexes $\text{Zn19}$ and $\text{Zn21}$ displayed similar low fluorescence quantum yields ($\Phi_{fl} = 0.006$ and 0.007 respectively), but complex $\text{Zn20}$ emitted strongly with a ~50 fold increase ($\Phi_{fl} = 0.36$). Analogous differences were found for the excited state lifetime as determined by transient absorbance spectroscopy. A lifetime of 90 ± 10 ps was obtained for $\text{Zn19}$ whereas a lifetime of 3 ± 1 ns was observed for $\text{Zn20}$. The transient absorbance data revealed significant differences between $\text{Zn19}$ and $\text{Zn20}$. At very short times (0.5 ps) following the laser pulse, $\text{Zn19}$ and $\text{Zn20}$ displayed similar transient absorbance difference spectra that contained bleaching of the ground state bands and excited state stimulated emission. The initial spectrum of each complex was assigned to that of the Franck-Condon form of the $S_1$ excited state that underwent vibrational cooling over 9 ± 3 ps and 25 ± 5 ps respectively and formed a relaxed excited state. The relaxed $S_1$ excited state of $\text{Zn19}$ subsequently decayed with a 90 ps time constant and the lifetime was dominated by internal conversion to the ground state. In contrast, the relaxed $S_1$ excited state of $\text{Zn20}$ decayed in ca. 3 ns. The decay included repopulation of the ground state but also formation (~ 30 % yield) of a longer-lived transient state. The authors ascribed the long-lived transient to the lowest triplet excited state. Thus, hindered rotation of the $meso$ aryl rings with respect to the dipyrrin framework (by the mesityl moiety in $\text{Zn20}$ compared to the phenyl group in $\text{Zn19}$ substantially slowed non-radiative relaxation to the ground state. Consequently the bis(dipyrrinato)zinc(II) complex was transformed from a weakly emissive and rapidly deactivating system to a strongly emitting complex with a multi-nanosecond excited state lifetime.
Figure 5  Bis(dipyrrinato)metal(II) complexes, 19, 20, 21.
5.1.4 Borondifluoride dipyrrins

Borondifluoride dipyrrin complexes, boradiazaindacene dyes, $N,N'$-difluoroboryl dipyrrins or 4,4-difluoro-4-bora-3a,4a-diaza-s-indacenes are comprised of only one dipyrrin ligand complexed to a borondifluoride moiety and shall be abbreviated hereafter as BODIPY. This type of dipyrrin complex is the most popular of the dipyrrin complexes owing to their applications as biological fluorescent labels, probes and in lasing applications. The basic spectroscopic characteristics of BODIPY complexes were overviewed in chapter 1 and substantial reviews of these dyes also exist. Briefly, their characteristics include moderately strong ($\varepsilon = 40,000 - 100,000 \text{ M}^{-1} \text{ cm}^{-1}$) and sharp (FWHM ca. 25 nm) blue-green absorbance centred around 500 nm, Stokes shifts in the range 500 – 900 cm$^{-1}$ and fluorescence lifetimes of ca. 5 ns. The fluorescent properties of BODIPYs can be tuned preparatively by introduction of functional substituents on the dipyrrin framework, replacing the meso-CH position with a nitrogen bridge to create azadipyrromethenes, or by substitution of the fluorine atoms.

A series of meso substituted BODIPY dyes were synthesised for inclusion in light harvesting arrays, however they were found to be only weakly fluorescent when compared to a commercially available BODIPY complex. Commercially available BODIPY dyes are generally substituted at the β position of the pyrrole ring (Fig. 6). Complex 23 displayed an absorbance $\lambda_{\text{max}}$ at 516 nm and emission maximum at 535 nm. The quantum yield for fluorescence was 0.058 in toluene and the singlet excited state lifetime consisted of a fast component (15 ± 4 ps) attributed to excited state relaxation dynamics followed by a short lifetime of 520 ± 50 ps. This was in contrast to the intense fluorescence of the commercial β-substituted BODIPY dye 22 ($\Phi_{\text{fl}} = 0.51$, $\tau = 5000 \pm 30$ ps).
Consequently the BODIPYs 24 – 27 (Fig. 7) were prepared to investigate if modification of the meso substituent would increase fluorescence yields as was observed for the bis(dipyrrinato)zinc(II) complexes. In all compounds the boron-dipyrrin framework, which includes both pyrrole rings and the central six membered ring containing the boron atom were essentially planar. One of the most pronounced effects of the meso aryl moiety was observed in the dihedral angle between the meso aryl ring and the planes defining various dipyrrin elements. The angle increased from ~60 ° and ~50 ° for 24 and 25 where no steric hindrance for aryl rotation was present, to ~85 ° and ~75 ° for 26 and 27 when motion was restricted. Regardless of the presence or nature of the meso substituent all of the UV-vis ground state absorbance spectra contained a $S_0 \rightarrow S_1$ transition with a $\lambda_{\text{max}}$ between 490 – 500 nm and vibronic components spanning ca. 25 nm to higher energy. A parallel transition ($S_1 \rightarrow S_0$) existed in the fluorescence spectra with standard Stokes shift observed (500 – 900 cm$^{-1}$). Although the substituents on the aryl ring of the BODIPYs had only modest impact on the absorbance and fluorescence profiles, the nature of the aryl moiety had a profound effect on the fluorescence quantum yield and lifetime of the $S_1$ excited state. The fluorescence quantum yield and lifetime increased in order 24 ($\Phi_f = 0.062$, $\tau = 0.45$ ns), 25 ($\Phi_f = 0.069$, $\tau = 0.55$ ns), 26 ($\Phi_f = 0.93$, $\tau = 5.8$ ns) and 27 ($\Phi_f = 0.93$, $\tau = 6.6$ ns). Low emission yield and short excited state lifetimes obtained for aryl substituted complexes without steric hindrance (24 and 25) indicated a facile $S_1$ excited state non radiative decay that was restricted when steric constraints were imposed (26 and 27). Transient absorbance data and theoretical calculations showed the short excited state lifetimes resulted from excited state conformational changes that drove fast internal conversion to the ground state.
Compounds containing both a chromophore and a redox group incorporated into a single molecule have been extensively studied. Four different types of covalently linked BODIPY-ferrocene conjugates (28 – 31, Fig. 8) were synthesised following several different routes. The compounds 28 – 31 exhibit characteristic UV-vis absorbance spectra with a characteristic strong band in the region 520 – 560 nm, which corresponded to the $S_0 \rightarrow S_1$ transition, with a vibronic overtone at higher energy. An ill-defined band at ca. 400 nm was attributed to the $S_0 \rightarrow S_2$ transition. For conjugates 28 – 30 an additional broad band was observed in the region 660 – 680 nm. The low energy band was assigned to the intramolecular charge transfer transition, which was very intense for compound 29 that possessed two ferrocenyl moieties. The charge transfer band was not observed for compound 31 where the conjugation between the BODIPY and ferrocene group was less effective. All compounds showed negligible fluorescence supporting rapid photoinduced electron transfer from the donor ferrocenyl group(s) to the acceptor boron-dipyrrin unit. However fluorescence was restored through preclusion of electron transfer from the ferrocene to the BODIPY moiety. Oxidation of the ferrocene unit to the ferricenium ion in conjugates 28 and 29 was achieved by chemical oxidation and changes in both the absorbance and emission spectra were monitored. When 29 was oxidised, the charge transfer band at 682 nm in the UV-vis spectrum decreased in intensity until it disappeared while the $S_0 \rightarrow S_1$ band increased in intensity, broadened and shifted to higher wavelength with an isobestic point at 640 nm. Concomitantly emission was restored and a strong fluorescence band at 612 nm with a shoulder at longer wavelength was observed. A singlet state lifetime of 5.2 ns with a quantum yield of 0.31 was observed for 29. Thus by...
oxidation of the ferrocenyl moiety and elimination of the electron transfer pathway, the fluorescence of the BODIPY dyes can be “switched on” and by analogy reduction will “switch off” fluorescence.

![Chemical structures](image)

**Figure 8**  
_BODIPY-ferrocene conjugates, where Fc = ferrocene._

BODIPYs bearing ethynylpyrene units were constructed in a step by step procedure based on Pd(0) catalysed coupling reactions resulting in dual dye systems (32 – 34, Fig. 9). Molecular modelling studies and X-ray crystallography indicated that the pyrene unit was orthogonal to the borondifluoride dipyrrin unit in compounds 32, 33 and 34. The lowest energy conformation of 33 showed the phenylene and pyrene units were coplanar to each other but orthogonal to the BODIPY moiety. All compounds exhibited similar absorbance spectral characteristics. The absorbance spectrum of model compound 35, without a pyrene moiety, showed a strong $S_0 \rightarrow S_1$ ($\pi-\pi^*$) transition with a $\lambda_{max}$ at 527 nm ($\varepsilon = 60,000$ M$^{-1}$ cm$^{-1}$) attributed to the BODIPY chromophore. The less intense and relatively broad absorbance band located at $\lambda = 357$ nm was ascribed to the $S_0 \rightarrow S_2$ ($\pi-\pi^*$) transition also located on the BODIPY unit. The higher energy transition, $\lambda = 283$ nm, was assigned to the ($\pi-\pi^*$) transition localised on the phenyl-ethynyl subunit. The inclusion of a pyrene unit onto the BODIPY framework produced an absorbance spectral profile that was essentially the superposition of the spectra of the individual components. For compound 32, three bands are clearly observed at 230, 270 and _ca._ 340 nm, in addition to the BF$_2$-dipyrrin $S_0 \rightarrow S_1$ ($\pi-\pi^*$) and $S_0 \rightarrow S_2$ ($\pi-\pi^*$) transitions at $\lambda = 528$ and _ca._ 370 nm. The
former bands are assigned to \((\pi-\pi^*)\) transitions localised on the pyrene unit. The profile of 33 was similar to that of 32 except for a broadening of the \((\pi-\pi^*)\) transitions associated with the pyrene chromophores, while the profile of 34, with two pyrene units, possessed a set of intense transitions in the range \(\lambda = 340 – 480\) nm. No charge transfer absorbance bands were evident at long wavelengths. Fluorescence from the BODIPY fragment was apparent in all compounds and the emission profile showed good mirror symmetry with the corresponding absorbance band, with small Stokes shifts of \(ca. 600\) cm\(^{-1}\) observed. Fluorescence lifetimes of the BODIPY are generally in the range 4 – 7 ns. However both the quantum yield and fluorescence lifetime of 33 and 34 were reduced compared to 32.

For the directly linked dual dye, 32, the fluorescence excitation spectrum matched the absorbance spectrum exactly. In particular, photons absorbed by the pyrene-like moiety subunit were channelled to the BF\(_2\)-dipyrrin unit with high efficiency. No fluorescence was detected from the pyrene unit in the range 350 – 500 nm. The singlet lifetime and quantum yield were calculated to be 140 ns and 0.76 respectively, thus the pyrene based excited state in 32 was quenched by at least 100 fold and suggested a rate constant for energy transfer of 32 of \(> 10^{10}\) s\(^{-1}\). Both 33 and 34, following direct excitation into the pyrene based absorbance bands, resulted in very weak fluorescence at \(ca. 400 – 500\) nm where characteristic emission from ethynylated pyrene derivatives is observed. Excitation spectra recorded for emission from the BODIPY unit were consistent with fast energy transfer from the pyrene fragment. This showed that intramolecular energy transfer occurred with an efficiency of \(~95\) and \(90\%\) for 33 and 34 and energy transfer rates of \(3.0 \times 10^{10}\) s\(^{-1}\) and \(7 \times 10^9\) s\(^{-1}\) for the respective compounds were calculated. The authors also found that the two pyrene subunits in 34 acted as a single giant chromophores rather than two separate species.
Intense absorbance and emission from singlet states in the visible region are often desirable features for components in larger arrays. The ability to fine tune excited state characteristics via minor structural modifications of bis(dipyrrinato)metal(II) complexes and BODIPYs increases the number of applications for this class of compounds.
5.2 Abstract

This chapter serves as a preliminary investigation into the synthesis and photophysics of thienyl dipyrromethanes and dipyrrin complexes. By examination of the basic photophysical processes that occur in dipyrromethanes and dipyrrins with a meso thienyl moiety a greater understanding can be gained as to how these compounds may be included in larger supramolecular arrays.

The studies available in the literature clearly show that the electronic properties of a porphyrin macrocycle are greatly altered when six membered meso aryl groups are replaced with five membered aromatic heterocycles. Dipyrrromethanes / dipyrrins are porphyrinogenic molecules – precursors and side products. A perusal of the literature revealed that dipyrrin chemistry with five membered meso substituents has remained largely unexplored. There is however a wealth of information about dipyrrin complexes meso substituted with six membered phenyl ring.

Halper and Cohen investigated the effect of phenylacetylene rods attached to dipyrromethanes/dipyrrins at the meso position. The combination of the phenylacetylene groups with the dipyrrin moieties resulted in rich absorbance spectroscopy for the compounds. Lindsey et al. reported that restricted rotation of the meso aryl groups in BODIPYs and bis(dipyrrinato)metal complexes transformed very weakly emitting molecules into highly fluorescent chromophores. BODIPY-ferrocene conjugates which contain a redox group incorporated into the molecular framework of the chromophore have been synthesised. These complexes showed that when the ferrocene was attached to the molecular framework via a meso phenylethynyl moiety there was little or no communication between the two components. BODIPYs bearing pyrene units were also investigated. The compounds contained pyrene groups attached to different positions of the dipyrrin framework. Crystal structures of the molecule that possessed a meso phenylethynylpyrene group showed that the meso phenylethynylpyrene substituents were coplanar to each other but orthogonal to the dipyrrin framework. In all these cases the meso phenyl ring is expected to lie in a low energy conformation, an idealised orthogonal arrangement.
Studies on porphyrins have showed that \textit{meso} thienyl substituents lie in a co-planar arrangement with respect to the porphyrin macrocycle. The co-planar arrangement allows for overlapping of the two $\pi$ systems. The changes observed in the spectra of porphyrins (bathochromically shifted absorbance and emission spectra) are attributed to both the conformation which the thienyl groups adopt and the effect of the thiophene itself.

Thus a series of dipyrrromethanes were produced. The dipyrrromethanes are \textit{meso} substituted with a thien-2-yl moiety which is substituted at the thien-5-yl position with other aryl moieties. A preliminary study of the photophysics of the dipyrrromethanes and dipyrrins will be carried out.
5.3 Experimental
5.3.1 Materials

All manipulations were carried out under an atmosphere of argon or nitrogen using standard Schlenk techniques. All solvents were supplied by the Aldrich Chemical Company. Dichloromethane, chloroform, petroleum ether 40:60, pentane and hexane were dried over MgSO₄ prior to use. Diisopropylamine was distilled over potassium hydroxide before use. Methanol was distilled over magnesium turnings and iodine before use. 5-Bromo-2-thiophenecarboxaldehyde was purified by distillation using a Büchi Kügelrohr apparatus. Pyrrole was distilled over sodium hydroxide using a short path distillation apparatus prior to use. All other chemicals were obtained commercially and were used without further purification. Silica gel (Merck) was used as received. All mobile phases for column chromatography were dried over MgSO₄ before use. The preface “NB-” is applied to compound codes indicating that these are novel compounds synthesised throughout this work.

5.3.2 Equipment

¹H NMR and ¹³C NMR were recorded on a Bruker AC 400 spectrometer and Bruker ANC 600 spectrometer in CDCl₃ and were calibrated according to the residual solvent peak i.e. CHCl₃ at 7.26 ppm for all ¹H spectra and 77.16 ppm for all ¹³C spectra. Chemical shifts (δ) are given in parts per million (ppm). Proton coupling constants (J) are given in Hertz (Hz). Melting points were measured on a Stuart Scientific SMP1 melting point apparatus. IR spectra were recorded on a Perkin-Elmer 2000 FT-IR spectrophotometer (2 cm⁻¹ resolution) in a 0.1 mm sodium chloride liquid solution cell. All UV-vis spectra were measured on an Agilent Technologies 8453 photodiode array spectrometer using a 1 cm³ quartz cell. Emission spectra (accuracy ± 5 nm) were recorded at 298 K using a LS50B luminescence spectrophotometer, equipped with a red sensitive Hamamatsu R928 PMT detector, interfaced with Elonex PC466 employing Perkin-Elmer FL WinLab custom built software.
5.3.3 Synthesis

**General procedure for synthesis of compounds via the Sonogashira reaction.**

To a flame dried round bottom flask anhydrous triethylamine (~30 ml) was added and purged with nitrogen for 10 minutes. The halogenated aryl reactant was added and the solution was further purged for 5 minutes. A catalytic quantity of bis(triphenylphosphine) palladium(II)chloride, triphenylphosphine and cuprous iodide were added to the flask followed by an excess of aryl alkyne in quick succession. The reaction mixture was refluxed overnight under an inert atmosphere then allowed to cool. Solvent and excess aryl alkyne was removed under reduced pressure. The crude product was extracted from the oil by adding CH$_2$Cl$_2$ (ca. 5 ml) followed by the addition of petroleum ether (or hexane) (ca. 25 ml). The solvent was then decanted off. This extraction process was repeated several times until the organic layer remained colourless. The organic layers were combined and dried over magnesium sulphate. The solvent was then removed via rotary evaporation affording a dark residue. The crude product was purified by column chromatography as described for each individual compound.

**General procedure for the preparation of meso substituted dipyrromethanes.**

*Meso* substituted dipyrromethanes were prepared via a one-step synthetic route similar to that described by Lindsey et al.\(^9\) Pyrrole (25 equivalents) and the appropriate aldehyde (1 equivalent) were added to a dry round bottom flask and degassed with nitrogen for 10 minutes. Trifluoroacetic acid (0.1 equivalents) was then added and the solution stirred for 5 minutes under an inert atmosphere at room temperature and then quenched with 0.1 M NaOH. Ethyl acetate was added and the organic phase was washed with water and dried over magnesium sulphate. The solvent was removed under reduced pressure to afford an oil. The crude product was purified using a Kügelrohr or by column chromatography to give the pure dipyrromethane as a solid.
5.3.3.1 5-(Naphthalenylethynyl)thiophene-2-carboxaldehyde (NB-A8)

\[
\text{H} + \text{Br} - \text{S} - \text{H}
\]

\[
\begin{array}{c}
6 \% \text{ Pd}([\text{PPh}_3]_2 \text{Cl}_2) \\
6 \% \text{ CuI} \\
12 \% \text{ PPh}_3
\end{array}
\]

\[
\text{Et}_3\text{N}, \Delta, \text{N}_2
\]

5-(Naphthalenylethynyl)thiophene-2-carboxaldehyde was prepared via the Sonogashira reaction. 5-Bromo-2-thiophenecarboxaldehyde (1.0 mmol, 0.12 ml), bis(triphenylphosphine)palladium(II)chloride (0.06 mmol, 42 mg, 6 %), triphenylphosphine (0.12 mmol, 31 mg, 12 %), cuprous iodide (0.06 mmol, 11 mg, 6 %) and 1-ethynlnaphthalene (1.25 mmol, 0.18 ml) were used. The crude product was purified by column chromatography using silica gel and a mobile phase of CH$_2$Cl$_2$ : petroleum ether 40:60 (50 : 50) which afforded a yellow solid. Yield: 192 mg, 0.73 mmol, 73 %.

$^1$H NMR (400 MHz, CDCl$_3$): 9.91 (1H, s), 8.33 (1H, d, $J = 8.4$ Hz), 7.90 (2H, t, $J = 7.6$ Hz), 7.80-7.78 (1H, m), 7.73 (1H, d, $J = 4$ Hz), 7.66-7.61 (1H, m), 7.59-7.54 (1H, m), 7.51-7.47 (1H, m), 7.43 (1H, d, $J = 4$ Hz) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): 182.45, 143.99, 136.17, 133.16, 132.97, 132.93, 132.56, 131.05, 130.01, 128.51, 127.27, 126.76, 125.86, 125.29, 119.48, 96.28, 86.67 ppm. IR (CH$_2$Cl$_2$): (C≡C) 2204 cm$^{-1}$. m.p.: 85-86 °C
5.3.3.2 5-(Phenanthren-9-ylethynyl)thiophene-2-carboxaldehyde (NB-A9)

5-(Phenanthren-9-ylethynyl)thiophene-2-carboxaldehyde was prepared via the Sonogashira method. 5-Bromo-2-thiophenecarboxaldehyde (1.0 mmol, 0.12 ml), bis(triphenylphosphine)palladium(II)chloride (0.06 mmol, 42 mg, 6 %), triphenylphosphine (0.12 mmol, 31 mg, 12 %), cuprous iodide (0.06 mmol, 11 mg, 6 %) and 9-ethynylphenanthrene (1.25 mmol, 253 mg) were used. The crude product was purified by column chromatography using silica gel and CH$_2$Cl$_2$ : hexane (45 : 55) which afforded a yellow solid. Yield: 256 mg, 0.82 mmol, 82 %.

$^1$H NMR (400 MHz, CDCl$_3$): 9.90 (1H, s), 8.72-8.69 (1H, m), 8.67 (1H, d, $J = 8$ Hz), 8.43-8.40 (1H, m), 8.12 (1H, s), 7.89 (1H, d, $J = 8$ Hz), 7.74-7.68 (4H, m), 7.62 (1H, t, $J = 7.4$ Hz), 7.44 (1H, d, $J = 3.6$ Hz) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): 182.46, 144.04, 136.17, 132.92, 132.66, 130.97, 128.88, 128.15, 127.42, 127.36, 127.21, 126.65, 122.96, 122.73, 118.32, 96.49, 86.30 ppm. IR (CH$_2$Cl$_2$): 2198 (C≡C) cm$^{-1}$. m.p.: 173-174 ºC
1-Trimethylsilyl ethynylpyrene was prepared via the Sonogashira reaction. 1-Bromopyrene (1.06 mmol, 300 mg), bis(triphenylphosphine) palladium(II)chloride (0.13 mmol, 91 mg, 12 %), triphenylphosphine (0.25 mmol, 65 mg, 24 %), cuprous iodide (0.13 mmol, 24 mg, 12 %) and trimethylsilylacetylene (2.10 mmol, 0.29 ml) were used. The solution was heated to 60 ºC and stirred overnight under an inert atmosphere. [Note: Due to the volatile nature of the TMSacetylene the flow of nitrogen should be sufficiently lowered for the course of the reaction.] The crude product was purified by column chromatography using silica gel and petroleum ether 40:60 (100 %) as mobile phase which afforded a pale yellow solid. Yield: 177 mg, 0.59 mmol, 56 %. Spectroscopic data were in good agreement with reported data.

\(^1\text{H NMR}\) (400 MHz, CDCl\textsubscript{3}): 8.56 (d, 1H, \(J = 8.8\) Hz), 8.23-7.99 (m, 8H), 0.39 (s, 9H) ppm. m.p.:102 - 103 ºC
5.3.3.4 1-Ethynylpyrene

1-Ethynylpyrene was prepared by deprotection reaction as described by Austin et al.\textsuperscript{34} Trimethylsilylethynylpyrene (2.01 mmol, 600 mg) was dissolved in dry methanol (~15 ml) and a small amount of dry CH\textsubscript{2}Cl\textsubscript{2} (~3 ml) to aid dissolution. K\textsubscript{2}(CO\textsubscript{3}) \textsubscript{3} (0.20 mmol, 28 mg) was added and the solution was stirred for 3 hours during which time a cream coloured precipitate formed. The solvent was removed under reduced pressure and the resulting cream solid was dissolved in CH\textsubscript{2}Cl\textsubscript{2} (~60 ml) and washed with aliquots of 5\% NaHCO\textsubscript{3} (4 x 25 ml). The organic phase was extracted, dried over MgSO\textsubscript{4} and solvent removed \textit{via} rotary evaporation affording a beige solid. Yield: 403 mg, 1.78 mmol, 88\%. Spectroscopic data were in good agreement with reported data. Error! Bookmark not defined.

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): 8.72 (d, 1H, J = 8.8 Hz), 8.29-8.23 (m, 4H), 8.17-8.14 (m, 2H), 8.10-8.05 (m, 2H), 3.65 (s, 1H) ppm. m.p.: 100 - 101 °C
5.3.3.5 5-(Pyrenylethynyl)thiophene-2-carboxaldehyde (NB-A10)

5-(Pyrenylethynyl)thiophene-2-carboxaldehyde was prepared via the Sonogashira reaction. Diisopropyamine (20 ml), 1-ethynylpyrene (1.0 mmol, 226 mg), bis(triphenylphosphine) palladium(II) chloride (0.06 mmol, 42 mg, 6%), triphenylphosphine (0.12 mmol, 31 mg, 12%), cuprous iodide (0.06 mmol, 11 mg, 6%) and 5-bromo-2-thiophenecarboxaldehyde (1.0 mmol, 0.12 ml) were used. The reaction mixture was stirred overnight under an inert atmosphere. The crude product was purified by column chromatography on silica gel using CH$_2$Cl$_2$: pentane (70 : 30) as mobile phase which afforded a yellow-orange solid. Yield: 282 mg, 0.84 mmol, 84%.

$^1$H NMR (400 MHz, CDCl$_3$): 9.92 (1H, s), 8.54 (1H, d, $J = 8.8$ Hz), 8.26-8.03 (8H, m), 7.74 (1H, d, $J = 4$ Hz), 7.47 (1H, d, $J = 4$ Hz) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): 183.04, 133.13, 132.51, 132.10, 132.06, 131.18, 130.96, 129.67, 128.93, 128.85, 127.22, 126.48, 126.09, 126.04, 125.09, 124.61, 124.41 96.45, 81.77 ppm. IR (CH$_2$Cl$_2$): (C≡C) 2197 cm$^{-1}$. m.p.: 122-123 ºC.
5.3.3.6 5-(Ferrocenylethynyl)thiophene-2-carboxaldehyde (NB-A11)

\[
\text{Fe} \equiv \text{H} + \text{Br-S-CH}_{2}\text{CO} \rightarrow \\
6 \% \text{Pd(PPh}_{3}\text{)}_{2}\text{Cl}_{2} \quad \text{Et}_{3}\text{N}, \Delta, \text{N}_{2} \quad 6 \% \text{CuI} \quad 12 \% \text{PPh}_{3}
\]

5-(Ferrocenylethynyl)-2-thiophenecarboxaldehyde was prepared via the Sonogashira reaction. 5-Bromo-2-thiophenecarboxaldehyde (1 mmol, 0.12 ml), bis(triphenylphosphine)palladium(II)chloride (0.06 mmol, 42 mg, 6 %), triphenylphospine (0.12 mmol, 31 mg, 12 %), cuprous iodide (0.06 mmol, 11 mg, 6 %) and ethynylferrocene (1.25 mmol, 263 mg) were used. The crude product was purified by column chromatography using silica gel and CH\(_2\)Cl\(_2\) : petroleum ether 40:60 (50 : 50) which afforded a red solid. Yield: 273 mg, 0.73 mmol, 73 %.

\(^{1}\text{H NMR}\) (400 MHz, CDCl\(_3\)): 9.85 (1H, s), 7.64 (1H, d, \(J = 4\) Hz), 7.22 (1H, d, \(J = 4\) Hz), 4.62-4.58 (2H, m), 4.38-4.34 (2H, m), 4.31 (5H, s) ppm. \(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)): 182.38, 142.92, 136.35, 134.02, 131.64, 98.67, 78.54, 71.73, 70.22, 69.69 ppm. \(\text{IR}\) (CH\(_2\)Cl\(_2\)): (C≡C) 2209 cm\(^{-1}\). \text{m.p.}: 157-158 °C.
5.3.3.7 *Meso* (phenyl)dipyromethane (Ph-DPM)

*Meso* (phenyl)dipyromethane was prepared *via* a procedure described by Lindsey et al. Pyrrole (125 mmol, 8.67 mmol), benzaldehyde (5 mmol, 0.51 ml) and trifluoroacetic acid (0.5 mmol, 0.04 ml) were used. The crude product was purified by column chromatography using silica gel and neat CH$_2$Cl$_2$ as mobile phase which afforded an off-white solid. Yield: 0.37 g, 1.66 mmol, 33%. Spectroscopic data were in good agreement with reported data.$^9$

$^1$H NMR (400 MHz, CDCl$_3$): 7.90 (2H, br s), 7.35-7.18 (5H, m), 6.71-6.67 (2H, m), 6.19-6.16 (2H, m), 5.93-5.91 (2H, m), 5.47 (1H, s) ppm. m.p.: 98 – 99 °C.
Meso (mesityl)dipyrromethane was prepared via a procedure described by Lindsey et al. Pyrrole (125 mmol, 8.67 ml), mesitylaldehyde (5 mmol, 0.74 ml) and trifluoroacetic acid (0.5 mmol, 38 µl) were used. The crude product was purified by using a Kügelrohr (170 °C, 0.04 mm Hg) which afforded a yellow solid. Yield: 0.35 g, 1.32 mmol, 26 %. Spectroscopic data were in good agreement with reported data.  

$^1$H NMR (400 MHz, CDCl$_3$): 7.94 (2H, br s), 6.86 (2H, s), 6.67-6.65 (2H, m), 6.18-6.16 (2H, m), 6.01-5.99 (2H, m), 5.92 (1H, s), 2.27 (3H, s), 2.05 (6H, s) ppm. m.p.: 174 - 175 °C
5.3.3.9 *Meso* (thien-2-yl)dipyromethane (NB-DPM-1)

![Chemical structure of NB-DPM-1](image)

*Meso* (thien-2-yl)dipyromethane was prepared according to the method reported by Maiti et al.\textsuperscript{14} Pyrrole (64.9 mmol, 4.5 ml) and 2-thiophenecarboxaldehyde (10.7 mmol, 1 ml) were added to a round bottom flask and purged with argon for 10 minutes. Trifluoroacetic acid (1.1 mmol, 84 µl) was added and the solution was stirred for 30 minutes. The reaction was quenched with a molar excess of triethylamine (~1 ml), extracted into ethyl acetate, washed with water and dried over MgSO\textsubscript{4}. Excess pyrrole and solvent was removed under reduced pressure resulting in red oil. The crude product was purified by column chromatography on silica gel using CH\textsubscript{2}Cl\textsubscript{2} : Pet. Ether 40:60 (40 : 60) as mobile phase affording a pale yellow solid. Yield: 0.94 g, 4.11 mmol, 38 %. Spectroscopic data were in good agreement with reported data.\textsuperscript{13,14}

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): 7.99 (1H, br s), 7.23-7.22 (1H, m), 6.97-6.95 (1H, m), 6.90-6.89 (1H, m), 6.70-6.68 (2H, m), 6.19-6.17 (2H, m), 6.06-6.04 (2H, m), 5.57 (1H, s) ppm.
Meso (5-bromothien-2-yl)dipyrrromethane (NB-DPM-2)

\[
\begin{align*}
\text{H} & \quad + \quad \text{H} \\
\text{N} & \quad \text{O} \\
\text{S} & \quad \text{Br} \\
\text{Br}
\end{align*}
\]

Meso (5-bromothien-2-yl)dipyrrromethane was prepared according to the method reported by Maiti et al.\(^{14}\) Pyrrole (6 mmol, 0.41 ml), 5-bromothiophene-2-carboxaldehyde (1 mmol, 12 ml) and trifluoroacetic acid (0.2 mmol, 15 µl) were used. The crude product was purified by column chromatography on silica gel using CH\(_2\)Cl\(_2\) : Pet. Ether 40:60 (50 : 50) as mobile phase which afforded a pale yellow solid. Yield: 104 mg, 0.34 mmol, 34 %

\(^1\)\text{H NMR} (400 MHz, CDCl\(_3\)): 7.98 (2H, br s), 6.89 (1H, d, \(J = 3.6\) Hz), 6.72-6.69 (2H, m), 6.63 (1H, d, \(J = 3.6\) Hz), 6.18-6.16 (2H, m), 6.06-6.05 (2H, m), 5.65 (1H, s) ppm.
5.3.3.11  *Meso* (5-(trimethylsilylethynyl)thien-2-yl)dipyrromethane
(NB-DPM-3)

*Meso* (5-(trimethylsilylethynyl)thien-2-yl)dipyrromethane was prepared *via* Lindsey’s synthetic method. Pyrrole (12 mmol, 0.83 ml), 5-trimethylsilylethynyl-2-thiophenecarboxaldehyde (0.48 mmol, 100 mg) and trifluoroacetic acid (0.05 mmol, 4 µl) were used. The crude product was purified by column chromatography using silica gel and CH$_2$Cl$_2$ : Et$_3$N (99 : 1) as mobile phase which afforded a brownish yellow solid. Yield: 42 mg, 0.13 mmol, 27 %.

$^1$H NMR (400 MHz, CDCl$_3$): 7.89 (2H, br s), 7.11 (1H, d, $J = 3.6$ Hz), 6.74 (1H, dd, $J = 2.8$, 1.2 Hz), 6.69-6.67 (2H, m), 6.30-6.28 (2H, m), 6.08-6.05 (2H, m), 5.64 (1H, s) 0.26 (9H, s) ppm.
5.3.3.12  *Meso* (5-ethynylthien-2-yl)dipyrrromethane (NB-DPM-4)

*Meso* (5-ethynylthien-2-yl)dipyrrromethane was prepared by a deprotection reaction as described in literature.\(^\text{34}\) *Meso* (5-(trimethylsilylthienyl)thien-2-yl)dipyrrromethane (0.23 mmol, 75 mg) was added to dry methanol (~15 ml) along with anhydrous K\(_2\)(CO\(_3\)) (0.05 mmol, 6 mg) and the reaction mixture allowed to stir overnight under an inert atmosphere. The solvent was removed under reduced pressure. The crude product was dissolved in CH\(_2\)Cl\(_2\) and washed with aliquots of 5 % NaHCO\(_3\) (3 x 50 ml). The organic phase was extracted and dried over MgSO\(_4\). Removal of solvent under reduced pressure which afforded a light brown solid. Yield: 41 mg, 0.16 mmol, 71 %

\(^1\)H NMR (400 MHz, CDCl\(_3\)): 8.02 (2H, br s), 7.11 (1H, d, J = 3.6 Hz), 6.74-6.73 (1H, m), 6.71-6.69 (2H, m), 6.16 (2H, m), 6.06-6.03 (2H, m), 5.68 (1H, s) 3.32 (1H, s) ppm.
Meso (5-(phenylethynyl)-thien-2-yl)dipyrrromethane (NB-DPM-5)

Meso (5-(phenylethynyl)thien-2-yl)dipyrrromethane was prepared via Lindsey’s method. Pyrrole (26.5 mmol, 1.9 ml), 5-(phenylethynyl)-2-thiophenecarboxaldehyde (1.06 mmol, 225 mg) and trifluoroacetic acid (0.11 mmol, 8 µl) were used. The crude product was purified by column chromatography on silica gel using CH$_2$Cl$_2$:Et$_3$N (99:1) as mobile phase which afforded a yellowish brown solid. Yield: 149 mg, 0.45 mmol, 43%.

$^1$H NMR (400 MHz, CDCl$_3$): 8.03 (2H, br s), 7.50-7.47 (2H, m), 7.35-7.33 (3H, m), 7.13 (1H, d, $J = 3.6$ Hz), 6.78 (1H, d, $J = 3.6$ Hz), 6.71-6.70 (2H, m), 6.19-6.15 (2H, m), 6.08 (2H, m), 5.69 (1H, s) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): 146.85, 130.71, 130.58, 130.33, 130.30, 127.34, 124.58, 121.82, 121.35, 116.67, 107.48, 107.03, 106.24, 92.10, 81.67 ppm.
5.3.3.14 *Meso* 5-(naphthalenylethynyl)thien-2-yl)dipyrromethane  
(NB-DPM-6)

*Meso* 5-(naphthalenylethynyl)thien-2-yl)dipyrromethane was prepared *via* Lindsey’s method. Pyrrole (19 mmol, 1.32 ml), 5-(naphthalenylethynyl)-2-thiophenecarboxaldehyde (0.76 mmol, 200 mg) and trifluoroacetic acid (0.076 mmol, 6 µl) were used. The crude product was purified by column chromatography using silica gel and CH$_2$Cl$_2$: Et$_3$N (99:1) as mobile phase which afforded a dark solid. Yield: 89 mg, 0.24 mmol, 31%.

$^1$H NMR (400 MHz, CDCl$_3$): 8.32 (1H, d, $J$ = 8.4 Hz), 8.11 (2H, br s), 7.83 (2H, t, $J$ = 8.6 Hz), 7.69 (1H, m), 7.59-7.51 (2H, m), 7.43 (1H, t, $J$ = 8.4 Hz), 7.22 (1H, d, $J$ = 4 Hz), 6.85-6.83 (1H, m), 6.74-6.72 (2H, m), 6.19-6.17 (2H, m), 6.10-6.09 (2H, m), 5.73 (1H, s) ppm.
Meso (5-(phenanthren-9-ylyethynyl)-thien-2-yl)dipyrromethane was prepared via Lindsey’s method. Pyrrole (8.80 mmol, 0.61 ml), 5-(phenanthren-9-ylyethynyl)thiophene-2-carboxaldehyde (0.35 mmol, 110 mg) and trifluoroacetic acid (0.035 mmol, 2.7 µl) were used. The crude product was purified by column chromatography using silica gel and CH$_2$Cl$_2$ : Et$_3$N (99 : 1) as mobile phase which afforded a dark yellowish solid. Yield: 36 mg, 0.08 mmol, 24 %.

$^1$H NMR (400 MHz, CDCl$_3$): 8.73-8.66 (2H, m), 8.43-8.40 (1H, m), 8.12 (1H, s), 7.90-7.88 (1H, m), 7.73-7.67 (5H, m), 7.44 (1H, d, $J = 4$ Hz), 6.75-6.73 (2H, m), 6.21-6.18 (2H, m), 6.12-6.09 (2H, m), 5.76 (1H, s) ppm.
Meso (5-(pyrenylethynyl)thien-2-yl)dipyrromethane (NB-DPM-8)

Meso (5-(pyrenylethynyl)-thien-2-yl)dipyrromethane was prepared according via Lindsey’s method. Pyrrole (37 mmol, 2.58 ml), 5-(pyrenylethynyl)thiophene-2-carboxaldehyde (1.5 mmol, 500 mg) and trifluoroacetic acid (0.15 mmol, 12 µl) were used. The crude product was purified by column chromatography on silica gel using CH₂Cl₂ : Et₃N (99 : 1) as mobile phase which afforded a brownish yellow solid. Yield: 142 mg, 0.31 mmol, 21 %

¹H NMR (400 MHz, CDCl₃): 8.55 (1H, d, J = 8.8 Hz), 8.24-8.01 (10H, m), 7.29 (1H, d, J = 3.6 Hz), 6.87 (1H, m), 6.76-6.74 (2H, m), 6.22-6.19 (2H, m), 6.13-6.11 (2H, m), 5.78 (1H, m) ppm.


5.3.3.17  

*Meso* (5-(ferrocenylethynyl)thien-2-yl)dipyrromethane  
(NB-DPM-9)

*Meso* (5-(ferrocenylethynyl)thien-2-yl)dipyrromethane was prepared via Lindsey’s method. Pyrrole (30 mmol, 2.08 ml), 5-(ferrocenylethynyl)thiophene-2-carboxaldehyde (1.2 mmol, 387 mg) and trifluoroacetic acid (0.12 mmol, 9 µl) were used. The crude product was purified by column chromatography on silica gel using CH$_2$Cl$_2$ : Et$_3$N (99 : 1) as mobile phase which afforded a reddish solid. Yield: 148 mg, 0.41 mmol, 34 %.

$^1$H NMR (400 MHz, CDCl$_3$): 8.00 (1H, br s), 7.05 (1H, d, $J = 3.6$ Hz), 6.76-6.74 (1H, m), 6.72-6.70 (2H, m), 6.19-6.17 (2H, m), 6.08-6.06 (2H, m), 5.69 (1H, s), 4.47-4.46 (2H, m), 4.25-4.24 (2H, m), 4.23 (5H, s) ppm.
Molar equivalents of *meso* (5-(phenylethynyl)thien-2-yl)dipyrrromethane (0.21 mmol, 68 mg) and dicobalt octacarbonyl (0.21 mmol, 70 mg) were added to nitrogen purged hexane (25 ml) with CH$_2$Cl$_2$ (~1 ml) added subsequently to aid dissolution of the dipyrrromethane. The reaction mixture was allowed to stir overnight under a nitrogen atmosphere, covered in tinfoil. The solvent was removed under reduced pressure resulting in a brown residue. The crude product was purified by column chromatography on silica gel using neat hexane followed by CH$_2$Cl$_2$ : hexane (75 : 25) affording a brown solid. Yield 138 mg, 0.23 mmol, 75%.

$^1$H NMR (400 MHz, CDCl$_3$): 8.08 (2H, br s), 7.66-7.64 (2H, m), 7.39-7.34 (3H, m), 7.19 (1H, d, $J = 4$ Hz), 6.78 (1H, d, $J = 4$ Hz), 6.74-6.73 (2H, m), 6.19-6.17 (2H, m), 6.09-6.08 (2H, m), 5.69 (1H, s) ppm. IR (CH$_2$Cl$_2$): $\nu$(CO) 2091, 2057, 2030 cm$^{-1}$.
5.3.3.19 *Meso* (5-(naphthalenylethynyl)thien-2-yl)dipyrrromethane dicobalt hexacarbonyl (NB-DPM-6-Co$_2$(CO)$_6$)

*Meso* (5-(naphthalenylethynyl)thien-2-yl)dipyrrromethane (0.13 mmol, 50 mg) and dicobalt octacarbonyl (0.18 mmol, 62 mg) were added to nitrogen purged hexane (25 ml) with CH$_2$Cl$_2$ (~1 ml). The reaction mixture was allowed to stir overnight under an inert atmosphere in the dark. The solvent was removed by rotary evaporation resulting in a dark brown residue. The crude product was purified by column chromatography on silica gel using CH$_2$Cl$_2$ : petroleum ether 40:60 (30 : 70) as mobile phase which afforded a brown solid. Yield: 75 mg, 0.11 mmol, 86%.

$^1$H NMR (400 MHz, CDCl$_3$): 8.02-7.99 (5H, m), 7.54-7.48 (2H, m), 7.44-7.39 (1H, m), 7.08 (1H, d, $J = 4$ Hz), 6.76 (1H, d, $J = 4$ Hz), 6.73-6.70 (2H, m), 6.18-6.16 (2H, m), 6.09-6.07 (2H, m), 5.68 (1H, s) ppm. IR (CH$_2$Cl$_2$): v(CO) 2090, 2058, 2028 cm$^{-1}$. 
Meso (5-(pyrenylethynyl)thien-2-yl)dipyrrromethane dicobalt hexacarbonyl (NB-DPM-8-Co₂(CO)₆)

Meso (5-(pyrenylethynyl)thien-2-yl)dipyrrromethane (0.89 mmol, 300 mg) and dicobalt octacarbonyl (0.89 mmol, 304 mg) were added to nitrogen purged hexane (25 ml) containing CH₂Cl₂ (~1 ml). The reaction mixture was allowed to stir overnight under an inert atmosphere in the dark. The solvent was removed under reduced pressure resulting in a brown residue. The crude product was purified by column chromatography using silica gel and neat hexane followed by neat CH₂Cl₂ as mobile phase. The solvent was removed immediately affording a light brown solid. Yield: 452 mg, 0.61 mmol, 92 %.

¹H NMR (400 MHz, CDCl₃): 8.36-8.01 (11H, m), 7.15 (1H, d, J = 3.6 Hz), 6.81 (1H, d, J = 3.6 Hz), 6.75-6.70 (2H, m), 6.17-6.15 (2H, m), 6.11-6.09 (1H, m), 5.71 (1H, s) ppm. IR (CH₂Cl₂): ν(CO) 2091, 2058, 2031 cm⁻¹.
Borondifluoride-(thien-2-yl)-dipyrrin was synthesised via an adapted literature method.\(^{35}\) A solution of CH\(_2\)Cl\(_2\) (50 ml) was purged with argon for 10 minutes charged with 2-thiophenecarboxaldehyde (1.0 mmol, 0.09 ml) and pyrrole (2.3 mmol, 0.16 ml) and further purged for 5 minutes. Trifluoroacetic acid (0.2 mmol, 15 µl) was added and the reaction mixture was allowed stir overnight under nitrogen. Subsequently a solution of DDQ (1.0 mmol, 227 mg) in CH\(_2\)Cl\(_2\) (10 ml) was added. The mixture was stirred at room temperature for an additional 30 minutes. Triethylamine (17.0 mmol, 2.37 ml) and BF\(_3\).OEt\(_2\) (18.6 mmol, 2.36 ml) were added, followed by stirring for 6 hours. The reaction mixture was washed with water and dried over MgSO\(_4\). The solvent was removed under reduced pressure resulting in a dark brownish orange residue. The crude product was purified by column chromatography on silica with CH\(_2\)Cl\(_2\) : hexane (50 : 50) as mobile phase which afforded an orange solid. Yield: 24 mg, 0.09 mmol, 9 %.

\(^1\)H NMR (400 MHz, CDCl\(_3\)): 7.7-7.67 (2H, m), 7.58-7.56 (1H, m), 7.40-7.38 (1H, m), 7.18-7.16 (1H, m), 6.97-6.96 (2H, m), 6.45-6.44 (2H, m) ppm.
Bis(thien-2-yl-dipyrrinato)zinc(II) complex was prepared according to Lindsey’s method.\textsuperscript{22} Freshly distilled THF (15 ml) was charged with \textit{meso} (thien-2-yl)dipyrromethane (0.87 mmol, 200 mg), an equimolar amount of \textit{p}-chloranil (0.87 mmol, 215 mg) and an excess of Zn(OAc)$_2$ (2.19 mmol, 402 mg). The reaction mixture was stirred overnight at room temperature. TLC analysis indicated that no dipyrromethane remained at that time. The solvent was removed under reduced pressure and the residue was dissolved in CHCl$_3$. The organic phase was washed with aqueous NaHCO$_3$ and water and dried (MgSO$_4$). The crude product was purified by column chromatography on silica gel using CHCl$_3$ : MeOH (98 : 2) affording an orange solid with a greenish surface lustre. Yield: 85 mg, 0.16 mmol, 38 %.

$^1$H NMR (400 MHz, CDCl$_3$): 7.54-7.53 (2H, m), 7.52-7.51 (4H, m), 7.42-7.40 (2H, m), 7.17-7.15 (2H, m), 7.04-7.03 (4H, m), 6.44-6.42 (4H, m) ppm.
5.4 Results

5.4.1 UV-vis absorbance studies

A UV-vis spectrum typical of a dipyromethane and bis(dipyrrinato)zinc(II) complex is displayed in figure 10. The electronic absorbance spectral features (λ_max) of the dipyromethanes synthesised in this study are listed in table 1. The absorbance spectrum of Ph-DPM has been previously reported in the literature.22

![Electronic absorbance spectra of tert-butylphenyl-DPM (-----) and bis(tert-butylphenyl-dipyrrinato)zinc(II) (––) recorded in CH₂Cl₂.](image)

<table>
<thead>
<tr>
<th>Compound</th>
<th>λ_max (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph-DPM</td>
<td>304, 422</td>
</tr>
<tr>
<td>Ms-DPM</td>
<td>316, 400</td>
</tr>
<tr>
<td>NB-DPM-1</td>
<td>314, 384, 428</td>
</tr>
<tr>
<td>NB-DPM-5</td>
<td>314, 330, 368, 466</td>
</tr>
<tr>
<td>NB-DPM-8</td>
<td>288, 310, 380, 402</td>
</tr>
<tr>
<td>NB-DPM-9</td>
<td>312, 364, 444</td>
</tr>
<tr>
<td>NB-BODIPY-1</td>
<td>286, 386, 484, 510</td>
</tr>
<tr>
<td>Bis(dipyrrinato-1)zinc(II)</td>
<td>344, 470, 492</td>
</tr>
</tbody>
</table>

Table 1 UV-vis absorbance data of dipyromethanes and dipyrrins recorded in CH₂Cl₂
A relatively small change was observed in the absorbance spectra of the dipyrromethanes when the *meso* substituent was a thiophene (Fig. 11). **NB-DPM-1** showed absorbance features that stretched further in to the red region of the spectrum compared to the phenyl derivatives. However when the conjugation of the *meso* substituent was extended as in **NB-DPM-5**, **NB-DPM-8** and **NB-DPM-9** a significant increase in the high energy transitions was observed. Both **NB-DPM-5** and **NB-DPM-9** displayed increased intensity in the transition centred at 314 and 312 nm respectively, attributed to $\pi-\pi^*$ transitions localised on the thienylethynyl unit. **NB-DPM-8** showed a dramatic increase in absorbance with transitions observed at 288, 310, 380 and 402 nm. By analogy with transitions observed by Ziessel et al.$^3$ these transitions were assigned to $\pi-\pi^*$ transitions localised on the *meso* thienylethynylpyrene component.

![Figure 11](image)

*Figure 11*  
*Electronic absorbance spectra of dipyrromethanes recorded in CH$_2$Cl$_2$.*
Following coordination to Co$_2$(CO)$_6$, the UV-vis spectrum of NB-DPM-8-Co$_2$(CO)$_6$, displayed broader less well-defined bands that stretched out as far as 700 nm (Fig. 12). The low intensity absorbance bands in the range 490 – 620 nm were tentatively assigned to d-d transitions.

![Electronic absorbance spectra of NB-DPM-8 (red line) and NB-DPM-8-Co$_2$(CO)$_6$ (blue line) recorded in CH$_2$Cl$_2$.](image)

**Figure 12**  
Electronic absorbance spectra of NB-DPM-8 (red line) and NB-DPM-8-Co$_2$(CO)$_6$ (blue line) recorded in CH$_2$Cl$_2$. 
There is a dramatic change in the absorbance spectrum upon formation of the borondifluoride analogue, NB-BODIPY-1 (Fig. 13). An intense absorbance band was observed at $\lambda = 510$ nm attributed to the $S_0 \rightarrow S_1$ ($\pi-\pi^*$) transition on the dipyrrin with a virronic overtone at ca. 484 nm. The $S_0 \rightarrow S_2$ ($\pi-\pi^*$) transition appeared at $\lambda = 386$ nm. A third band at higher energy ($\lambda = 286$ nm) was previously ascribed to a $\pi-\pi^*$ transition on the meso subunit. These transitions observed in the UV-vis spectrum agree well with those observed in other borondifluoride dipyrrin compounds.

![Electronic absorbance spectra of NB-DPM-1 (blue line) and NB-BODIPY-1 (red line) recorded in CH$_2$Cl$_2$.](image)

**Figure 13** Electronic absorbance spectra of NB-DPM-1 (blue line) and NB-BODIPY-1 (red line) recorded in CH$_2$Cl$_2$. 
The bis(dipyrrinato-1)zinc(II) complex displayed a $S_0 \rightarrow S_1$ transition with a $\lambda_{\text{max}}$ at 494 nm with a vibronic overtone at 470 nm (Fig. 14). This was attributed to a $\pi-\pi^*$ transition on the dipyrrin framework. The $S_0 \rightarrow S_2$ $\pi-\pi^*$ transition was observed at $\lambda = 354$ nm.

Figure 14 Electronic absorbance spectra of NB-DPM-1 (blue line) and bis(NB-dipyrrinato-1)zinc(II) (red line) in CH$_2$Cl$_2$. 
5.4.2 Steady state fluorescence studies

Room temperature emission studies of some of the compounds were carried out in CH$_2$Cl$_2$ (Fig. 15). Solutions were prepared such that they were isoabsorbtive at a selected wavelength having an optical density in solution of approximately 0.2 A.U. Ph-DPM, Ms-DPM, NB-DPM-1 and NB-DPM-9 were found to be only weakly emissive. The bromothiophene analogue, NB-DPM-2, showed increased fluorescence intensity as did NB-DPM-5. Table 2 below lists the emission maxima for the compounds studied.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{em}$</th>
<th>$\lambda_{exc}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph-DPM</td>
<td>356, 418</td>
<td>300</td>
</tr>
<tr>
<td>Ms-DPM</td>
<td>360, 516</td>
<td>315</td>
</tr>
<tr>
<td>NB-DPM-1</td>
<td>359</td>
<td>315</td>
</tr>
<tr>
<td>NB-DPM-5</td>
<td>380</td>
<td>315</td>
</tr>
<tr>
<td>NB-DPM-8</td>
<td>410, 430</td>
<td>400</td>
</tr>
<tr>
<td>NB-DPM-9</td>
<td>357</td>
<td>315</td>
</tr>
<tr>
<td>NB-DPM-8-Co$_2$(CO)$_6$</td>
<td>410, 430</td>
<td>400</td>
</tr>
</tbody>
</table>

Table 2  Fluorescence maxima of dipyrrromethanes and dicobalt hexacarbonyl complex recorded in CH$_2$Cl$_2$ at room temperature. Absorbance = 0.2 at excitation wavelength.
Figure 15  Steady-state emission spectrum of dipyrromethanes recorded in CH$_2$Cl$_2$ at room temperature ($\lambda_{exc} = 315$ nm, abs. = 0.2 at 315 nm).
Attachment of the fluorescent pyrenyl chromophore as in **NB-DPM-8** had a profound effect on the fluorescence of the dipyrromethane (Fig. 16). A substantial increase in the fluorescence intensity of the molecule was observed such that the emission silts were reduced by 75 % compared to all other dipyrromethanes. Two emission bands were observed at 408 and 430 nm typical of pyrene fluorescence.

![Figure 16](image)

**Figure 16** Steady-state emission spectrum of **NB-DPM-1** and **NB-DPM-8** recorded in CH$_2$Cl$_2$ at room temperature ($\lambda_{exc} = 315$ nm, abs. = 0.2 at 315 nm). Slits reduced by 75 % for **NB-DPM-8** in comparison to **NB-DPM-1**.
Following coordination of the dicobalt carbonyl moiety a reduction in emission intensity was observed (Fig. 17), however, there is no significant shift in the position of the band suggesting that the emission is ligand based without major MLCT contribution. The excitation spectra of the emissive compounds have the same profile as the corresponding absorbance spectra further suggesting that the emissive state is ligand based.

Figure 17  Steady-state emission spectra of NB-DPM-8 (blue line) and NB-DPM-8-Co$_2$(CO)$_6$ (red line) recorded in CH$_2$Cl$_2$ at room temperature ($\lambda_{exc} = 400$ nm, abs. = 0.2 at 400 nm).
5.4.3 Steady state photolysis

Broadband photolysis of the dicobalt hexacarbonyl complex, NB-DPM-1-Co$_2$(CO)$_6$, at $\lambda_{\text{exc}} > 520$ nm for 10 minutes resulted in bleaching of the parent bands at 2091, 2057 and 2030 cm$^{-1}$ and generation of weak product bands at 2062, 2023, 2006 and 1971 cm$^{-1}$ (Fig. 18). Subsequent photolysis at $\lambda_{\text{exc}} > 410$ nm for 10 minutes resulted in an obvious increase in the intensity of these bands indicative of increased formation of the pentacarbonyl species NB-DPM-1-Co$_2$(CO)$_5$(PPh$_3$)$_2$. Irradiation at $\lambda_{\text{exc}} > 320$ nm for 5 minutes caused further depletion of the parent bands. The product band at 2062 cm$^{-1}$ also underwent depletion which indicated that the pentacarbonyl photoproduction was also undergoing a photoreaction to produce the tetracarbonyl species, NB-DPM-1-Co$_2$(CO)$_4$(PPh$_3$)$_2$. Product bands in the final IR difference spectrum were observed at 1974, 1962 and 1937 (br) cm$^{-1}$, which are indicative of ($\mu_2$-alkyne)Co$_2$(CO)$_4$(L)$_2$ type species.$^{36}$

![Figure 18](image-url) **Infrared difference spectra following broadband irradiation of NB-DPM-1-Co$_2$(CO)$_6$ in hexane at $\lambda_{\text{exc}} > 520$ nm for 10 minutes (black lines, 10 minutes total irradiation), $\lambda_{\text{exc}} > 410$ nm for 10 minutes (red lines, 10 minutes total irradiation) and $\lambda_{\text{exc}} > 320$ nm for 5 minutes (blue lines, 5 minutes total irradiation).** Negative bands indicate bleaching of the parent complex while positive bands indicate formation of the pentacarbonyl and tetracarbonyl species.
Extended broadband photolysis of the dicobalt hexacarbonyl complex, **NB-DPM-8-Co$_2$(CO)$_6$**, at $\lambda_{exc} > 520$ nm for 30 minutes, $\lambda_{exc} > 410$ nm for 60 minutes and $\lambda_{exc} > 320$ nm for 60 minutes showed only minor depletion of the parent hexacarbonyl bands (Fig. 19). New bands were generated at 1970 and 1926 cm$^{-1}$, however these bands were not indicative of pentacarbonyl or tetracarbonyl photoproducts. As this is such a highly fluorescent complex it is possible that it does not undergo photosubstitution reactions. One possible cause for the generation of these bands is photodecomposition of the pyrenyl dipyrromethane complex.

![Figure 19 IR difference spectra following broadband irradiation of NB-DPM-8-Co$_2$(CO)$_6$ in hexane at $\lambda_{exc} > 520$ nm (black line, 30 minutes irradiation), $\lambda_{exc} > 410$ nm (red lines, 60 minutes total irradiation) and $\lambda_{exc} > 320$ nm (blue line, 60 minutes total irradiation).]
5.5 Discussion

The reaction at room temperature of an aldehyde in an excess of pyrrole, catalysed with TFA, afforded the meso substituted dipyrromethanes. The dipyrromethanes were purified by column chromatography. The dipyrromethanes were prepared in yields of 18 – 43 %.

The freebase dipyrromethanes were assessed for purity by TLC and characterised by \(^1\)H NMR. The \(^1\)H NMR spectra of all dipyrromethanes display complex coupling patterns derived from the protons on the dipyrromethylene unit in addition to those on the meso aryl substituent. For the freebase dipyrromethanes a broad singlet was observed in the region 7.90 – 8.66 ppm that corresponds to the N-H pyrrolic protons. This signal shifted slightly further downfield for meso thien-2-yl substituted dipyrromethanes as the conjugation of the meso substituent increased following the order: \textbf{NB-DPM-1} (7.99 ppm), \textbf{NB-DPM-5} (8.03 ppm), \textbf{NB-DPM-6} (8.32 ppm).

The peak related to CH on the methine bridge appeared at ca. 5.55 ppm. It is worthy of note that dipyrromethanes are highly unstable and should be subsequently reacted with due haste to form the more stable BODIPY or bis(dipyrrinato)metal complexes.

Dipyrromethanes are known to have a low intensity broad band in the high energy region of the UV-vis spectrum. The UV-vis spectra of the dipyrromethanes in this study showed similar absorbance bands. Absorbance bands with increased intensity were observed when the meso substituents was highly conjugated. These transitions were attributed to \(\pi-\pi^*\) transitions on the meso moiety rather than the dipyrromethane itself.

However the UV-vis spectra of the dipyrrin compounds, \textbf{NB-BODIPY-1} and \textbf{NB-bis(dipyrrinato-1)Zn(II)}, revealed new transitions that were characteristic of \(\pi-\pi^*\) transitions on the dipyrrin framework. The \(\lambda_{\text{max}}\) in each spectra (484 nm and 494 nm respectively) is bathochromically shifted with respect to borondifluoride phenylidipyrrin and bis(phenylidipyrinato)Zn(II). Comparison of the homoleptic complexes showed a bathochromic shifted by 7 nm. This is comparable to the shift observed between meso tetra phenyl and thienyl porphyrins, \textbf{ZnPp} \((\lambda_{\text{max}} = 419 \text{ nm})\) and \textbf{ZnTThP} \((\lambda_{\text{max}} = 429 \text{ nm})\). The conformation of the thienyl ring relative to the dipyrrin framework should be considered.
5.6 Conclusion

In this chapter experimental work was based on the synthesis of meso thien-2-yl dipyrrromethane compounds and some related dipyrrin and metal carbonyl complexes. Some initial photophysical measurements were taken. This work was a preliminary investigation into thienyl based dipyrrin systems.

The phenyl group lies approximately perpendicular to the plane of the dipyrrin. Consequently, the phenyl group in not in full conjugation with the pyrrolic system and substituents on the phenyl ring will have minimal influence on the \( \pi \) system of the dipyrrin.

The red shifted spectrum of tetra thienyl porphyrins has been attributed to the co-planar arrangement of the thienyl groups and porphyrins macrocycle. It is therefore likely this is the cause of the bathochromically shifted spectra of the dipyrrin complexes.

As observed in chapter 2 thienyl substitution of porphyrin systems altered the photophysical and electrochemical properties of the macrocycle, thus great promise lies in the potential of thienyl based dipyrrin complexes. Further work related to these systems is discussed in chapter six.
5.6 Bibliography


Chapter 6

Conclusions and future work

Chapter six provides a condensed review of the experimental findings from this study. A number of experiments that could be completed in order to advance our understanding of some of the photochemical processes that occurred in various chapters throughout this thesis are suggested.
6.1.1 Future work for chapter 2

Porphyrins NB-ZnP1 – NB-ZnP3 were synthesised with substituents at the thien-5-yl position. This induced bathochromic shifts in the UV-vis and fluorescence spectra. The absorbance spectra and FWHM values of the Soret band indicated that there was increased coupling of the thienyl and porphyrin π systems. A reduction in singlet and triplet lifetimes was observed which was in agreement with lifetime data published previously.

The thien-2-yl porphyrins substituted at the thien-4-yl position, NB-ZnP4 and NB-ZnP5 were very interesting. There was little of no change in their absorbance spectra with respect to ZnTThP. This indicated that the conjugation between the substituents on the thienyl moiety and the porphyrin macrocycle was not as effective as that observed in NB-ZnP1 – NB-ZnP3. However, there was a significant increased in the triplet lifetimes of both these porphyrins when compared to ZnTThP. This would suggest that the conformation of the thien-2-yl substituents with respect to the porphyrin macrocycle is changed when the meso thienyl rings are substituted at the thien-4-yl position and that caused the increase in lifetime as opposed to conjugation within the meso substituents. Future work should include obtaining a crystal structure of the porphyrins to check the conformation.

The phenyl porphyrins, NB-ZnP6 and NB-ZnP7, should adopt an idealised orthogonal arrangement with respect to the porphyrin plane and in doing so the π systems of the porphyrin and meso substituents will no longer overlap. The absorbance spectra of the phenyl porphyrins was bathochromically shifted with respect to ZnTPP and there was a significant change in the fluorescence profile although the lifetimes were only slightly altered. The most perceptible change was the triplet lifetime of NB-ZnP7 which was double that of ZnTPP. Clearly there is a contribution from the meso substituents even though the conformation prevents coupling of the π systems. A crystal structure of NB-ZnP7 would allow further analysis of the conformation of the meso substituents and therefore the degree of π overlap.
These results show that varying the structure in thienyl porphyrins does induce changes in the general types of spectra as well as the lifetimes associated with the excited states. The changes observed in the spectra of NB-ZnP4 – NB-ZnP7 are not a result of the increased coupling of the \( \pi \) systems. The crystal structures of these porphyrins will provide information about the conformation of the meso thienyl and phenyl rings with respect to the porphyrin macrocycle. This may prove that the increased lifetimes observed were due to the conformation of the porphyrin systems.

In this porphyrin study, the effect of conjugation vs. conformation was investigated for the porphyrins in series 2 (Fig. 1). The majority of the porphyrins depicted in figure 1 have been synthesised and their photophysical properties reported in chapter 2. The remaining porphyrins from series 1 and 3 (Fig. 1) should be synthesised and have their ground and excited states examined. The results obtained could then be compared to those reported for series 2. This would provide further experimental evidence to support the arguments discussed in this chapter.
In PDT of cancer, a photosensitiser, visible light and oxygen are combined to produce lethal agents which destroy or inactivate tumour cells. It is widely agreed that singlet oxygen is the primary cytotoxic agent responsible for the photobiological activity. Photosensitisers should exhibit the following properties: high extinction coefficients in the spectral region of excitation, a triplet state with appropriate energy to allow efficient energy transfer to ground state oxygen and long lived triplet state lifetimes ($\tau_T > 1 \mu s$) with high quantum yields ($\Phi_T > 0.4$). The quantum yield of singlet oxygen formation, $\Phi_\Delta$, is dependent on the quantum yield of the triplet state of the sensitisier, $\Phi_T$. Porphyrins **NB-ZnP7**, **NB-ZnP6** and to a lesser extent **NB-ZnP4** all possess triplet lifetimes that are sufficiently long to interact with ground state oxygen and generate singlet excited state oxygen. Future work on these porphyrins should include a quantum yield investigation of singlet oxygen generation.
6.1.2 Future work for chapter 3

Steady state photolysis, carried out in the dicobalt hexacarbonyl complexes, resulted in CO loss and quantum yields for the CO loss process indicated that the photochemical process is wavelength dependant. The quantum yield of CO loss was highest when the sample was irradiated at high energy ($\lambda_{\text{exc}} = 313$ and $365$ nm). At $405$ nm all quantum yields were found to be less than $5\%$. However the quantum yield increased with $\lambda_{\text{exc}} = 546$ nm. The CO loss process ranged from $5 – 23\%$. This was unexpected given that the absorbance bands at $546$ nm are weaker transitions than those at $405$ nm. This is a puzzling aspect to the quantum yields of CO loss and repeat experiments will need to be carried out to verify the validity of this result.

The photochemical activation of ($\mu_2$-alkyne)Co$_2$(CO)$_6$ complexes was studied by ps-TRIR and combined theoretical calculations allowed for the identification of the formation of a triplet diradical species, following excitation at $400$ nm and $532$ nm. The radical species rapidly recombined to regenerate the parent complex, with no evidence for CO loss arising from this species. Lifetimes for the triplet diradical species were in the range $38 – 71$ ps. The quantum yield of CO loss was low with $400$ nm irradiation. Future work to improve the competitiveness of the CO loss pathway may consist of the inclusion of a luminescent chromophore in the ($\mu_2$-alkyne)Co$_2$(CO)$_6$ complex. Coleman et al. reported that complexation of luminescent pyrene-thiophene dyads with Co$_2$(CO)$_6$ significantly quenched ligand based emission, possibly as a result of energy transfer from the luminescent pyrene moiety to the cobalt metal centre.\(^1\) A ps-TRIR investigation into such complexes would reveal whether this resulted in increased CO loss on the ps timescale.

The observation of competing pathways to CO loss allows for a better understanding of the photochemical properties of ($\mu_2$-alkyne)Co$_2$(CO)$_6$ complexes in developing a photochemically driven catalytic approach in the Pauson Khand reaction.
6.1.3 Future work for chapter 4

Picosecond TRIR studies were carried out on pyridine-W(CO)$_5$ in THF. Excitation of pyridine-W(CO)$_5$ at 400 nm resulted in photodissociation of the metal pentacarbonyl moiety with subsequent coordination to a solvent molecule within 1 ps. Over 100 ps, rearrangement of the initially formed $\sigma$ H bond between the tungsten pentacarbonyl and THF to the more stable (CO)$_5$Cr-$\eta^1$(O)THF photoproduct occurred. This is the first report detailing the rearrangement of metal pentacarbonyl species in THF solution. Further studies could include temperature dependant kinetics at 400 nm excitation and investigation of the reaction dynamics in other coordinating solvents. Pyridine-Cr(CO)$_5$ should also be investigated to delineate the effect of the Cr atom on the reaction kinetics.

Excitation of MPyTPP-Cr(CO)$_5$ at 532 nm resulted in photodissociation of the metal pentacarbonyl moiety, with subsequent coordination to a solvent molecule within 1 ps, and rearrangement of the initially formed $\sigma$ H bond between the chromium pentacarbonyl and the THF to the more stable (CO)$_5$Cr-$\eta^1$(O)THF photoproduct. This is surprising since at 532 nm it is the porphyrin S$_1$ excited state that is populated. The result would indicate that there is good communication between the porphyrin macrocycle and the metal pentacarbonyl even though they are connected through the pyridyl moiety which lies orthogonal to the porphyrin plane, thus preventing overlap of the $\pi$ systems. Further ps-TRIR studies should be carried out on the remaining porphyrin complexes at 532 nm in various solvents.

Irradiation of all porphyrin complexes at 400 nm resulted in formation of a porphyrin based excited state that decayed in less than 100 ps to regenerate the parent porphyrin complexes. Excitation at 400 nm of the porphyrin complexes would populate the S$_2$ state, rapid internal conversion to the S$_1$ excited state should occur. Thus the photochemistry was expected to be similar to that observed following 532 nm excitation. As TRIR only provides information about the carbonyl moiety, little information about the porphyrin excited state can be garnered from these results. There is a radial redistribution of electron density in the porphyrin macrocycle which results in less electron density on the metal (M = W or Cr).
This resulted in less backbonding on the carbonyl ligands thus the observed IR bands of the transient species were at higher energy. For both tungsten and chromium analogues evidence for both (THF)Cr(CO)$_5$ and (THF)W(CO)$_5$, were present in the final spectra (1 ns), *albeit* the IR bands were weak. Spectroelectrochemistry with IR detection should be carried out in order to aid the identification of the porphyrin excited state formed and the relaxation pathway it follows.
6.1.4 Future work for chapter 5

In view of the preliminary synthesis undertaken for meso thien-2-yl dipyrrromethanes, the synthesis of the borondifluoride dipyrrin complexes and bis(dipyrrinato)zinc(II) complexes is an attractive prospect. It is anticipated that the former complexes may possess unique photophysical properties typical of BODIPYs that is intense absorbance and fluorescence spectroscopy. The dipyrrromethane analogue, meso (5-pyrenylethynylthien-2-yl)dipyrrromethane, should form a BODIPY complex similar to that reported by Ziessel et al., with the meso phenyl moiety replaced by a thienyl group. Inefficient energy transfer from pyrene fragment to the BODIPY framework was observed by Ziessel attributed to the arrangement of the dipyrrin framework and the meso phenyl substituents.\(^2\) Similarly, the meso (5-ferrocenylethynylthien-2-yl)dipyrrromethane, should form a BODIPY complex similar to that reported by Rao and co-workers\(^3\) where the ferrocenyl moiety quenched the fluorescence of the complex but oxidation of the complex “switched on” the fluorescence. Of the dipyrrins produced by Rao et al. no fluorescence switching was observed for the complex that linked the ferrocene and dipyrrin through a meso phenylethynyl moiety. The authors ascribed this to lack of communication between the two components due to conformation. The combined studies of Rochford et al.\(^4\) and Brückner et al.\(^5\) of thienyl porphyrins showed considerable electronic communication between the thienyl and porphyrin \(\pi\) systems in both the ground and excited states. The relatively strong coupling of the two \(\pi\) systems was attributed in part to co-planar arrangement of the thienyl ring with respect to the porphyrin macrocycle. Assuming that the thienyl moiety would adopt a comparable co-planar arrangement with respect to the BODIPY framework, similar enhancements of both the ground and excited states should occur.
6.2 Bibliography


Appendix
A Sample preparation for laser flash photolysis.

All samples were prepared for laser flash photolysis in a quartz fluorescence cell which was attached to a glass degassing bulb. The appropriate porphyrin was dissolved in the appropriate spectrophotometric grade solvent and the solution was filtered to avoid the presence of light scattering particles. The concentration of porphyrin in each sample was adjusted so that the absorbance at the excitation wavelength ($\lambda_{\text{exc}} = 532$ or 355 nm) was $0.08 \pm 0.02$ absorbance units. The sample was then degassed by three cycles of a freeze-pump-thaw procedure to $10^{-3}$ Torr, followed by a substantial liquid pump phase in order to remove trace quantities of water and carbon dioxide not removed in the degassing procedure. One atmosphere of argon was then placed over the sample under the guidance of a pressure gauge.

Laser flash photolysis was carried out and monitored in the range of 800 – 300 nm, with the aid of filters for $\lambda > 500$, 400 and 320 nm to reduce excessive photodegradation of the sample. The UV-vis absorbance spectrum was recorded before and after each flash photolysis experiment and also after every 5 – 15 strikes of the laser (depending on sample sensitivity) to observed any possible spectral changes and to ensure sample stability.¹
For **NB-L2**, the irreversible oxidation of the thienyl group was observed at +1.78 V vs. Fc/Fc$^+$ (Fig. B1, a). No further oxidations were observed at higher potentials. Potential cycling over the peak potential produced deposition on the electrodes and the redox response became progressively distorted. The cyclic voltammogram of **NB-C2** (Fig. B1, b) contains the previously mentioned irreversible oxidation of the thienyl unit at approximately +1.72 V vs. Fc/Fc$^+$. A second irreversible oxidation wave is also observed at +0.88 V vs. Fc/Fc$^+$, and is assigned to the oxidation of the cobalt centre. The irreversible reduction of the metal centre is observed at -1.05 V vs. Fc/Fc$^+$. The radical anion then undergoes fast decomposition into several fragments including Co(CO)$_4^-$ as is evidenced by the oxidation at -0.13 V. This is in good agreement with the results published by Arnanz et al. Another new oxidation peak at -0.12 V and reduction peak at -0.77 V vs. Fc/Fc$^+$ were also observed and these are ascribed to decomposition products followed by reduction of the chemically adsorbed cobalt containing product on the electrodes.
Figure B1  Cyclic voltammogram of NB-L2 (a) and NB-C2 (b) showing oxidation and reduction waves.
The dithien-2-y lacetylene ligand, **NB-L3**, proved easier to oxidise than **NB-L1** and **NB-L2**. The single irreversible oxidation wave was observed at $E_{pa} = +1.47$ V vs. Fc/Fc$^+$ (Fig. B2, a). Zotti et al. reported the oxidation of dithien-2-y lacetylene at $E_{pa} = +1.07$ V.$^5$ However the authors used a different supporting electrolyte (0.1 M Et$_4$NClO$_4$) which may account for the difference in oxidation potential. Potential cycling over the peak potential caused rapid deposition onto the electrode indicating that material degradation (overoxidation) or electropolymerisation occurred. Cyclic voltammetry of the related complex **NB-C3** produced two irreversible oxidation waves due to the metal centre and thienyl moiety at +0.91 and +1.41 V vs. Fc/Fc$^+$ respectively (Fig. B2, b). The irreversible reduction of the cobalt occurred at -1.33 V vs. Fc/Fc$^+$. Continued sweeps indicated that the reduction process was followed by decomposition as the oxidation at +0.15 V is indicative of the oxidation of the Co(CO)$_4$ fragment. Further sweeps lead to loss of all characteristic oxidation and reduction potentials.
Figure B2  Cyclic voltammogram of NB-L3 (a) and NB-C3 (b) showing oxidation and reduction waves. The CV of NB-C3 shows loss of all wave definition due to electropolymerisation and/or overoxidation.
Cyclic voltammetry on NB-L4 provided a comparable oxidation wave at +1.55 V vs. Fc/Fc⁺ (Fig. B3, a). Successive redox cycles resulted in deposition on the working and counter electrode and caused loss of all wave definition. The CV of NB-C4 (Fig. B3, b) shows an irreversible oxidation due to the thienyl group at +1.58 V vs. Fc/Fc⁺ and the irreversible oxidation of the cobalt unit at +0.88 V vs. Fc/Fc⁺. The reduction of the metal centre was observed at -0.97 V vs. Fc/Fc⁺. In subsequent sweeps an oxidation at +0.17 V was observed along with a new small anodic peak at +0.59 V vs. Fc/Fc⁺ and two new cathodic waves at -0.22 V and -0.75 V. These smaller peaks, produced after the initial oxidation and reduction cycles, are a result of decomposition and deposition onto the working and counter electrodes.

*Figure B3*  Cyclic voltammogram of NB-L4 (a) and NB-C4 (b) showing oxidation and reduction waves.
The cyclic voltammogram of the bromothiophene analogue, **NB-L5**, also exhibits an irreversible oxidation process at +1.72V vs. Fc/Fc⁺ attributed to the oxidation of the thienyl moiety (Fig. B4, a). This is higher than the oxidation potential of the thiophene observed in **NB-L1** (+1.65 V vs. Fc/Fc⁺) where the 5’ position is occupied by a H atom rather than a Br. Displayed in figure B4 (b) is the cyclic voltammogram of **NB-C5**. As expected an irreversible oxidation is observed at +0.96 V vs. Fc/Fc⁺ of the coordinated Co carbonyl unit. This assignment is based on comparison with the peak position of Co₂(CO)₆ coordinated complexes observed by Esho et al.⁶ Irreversible oxidation of the thienyl moiety was observed at +1.76 V vs. Fc/Fc⁺. The irreversible reduction of the cobalt centre is displayed at -1.16 V vs. Fc/Fc⁺. In the subsequent sweep an oxidation wave attributed to Co(CO)₄⁻ at +0.15 V was observed along with the reduction at -0.74 V vs. Fc/Fc⁺ attributed to reduction of cobalt decomposition products on the electrode.
Figure B4  Cyclic voltammogram of **NB-L5** (a) and **NB-C5** (b) showing oxidation and reduction waves.
The cyclic voltammogram of the aldehydic complex, **NB-C6** (Fig. B5), possesses a positive potential at +0.99 V vs. Fc/Fc⁺ due to the irreversible oxidation of the cobalt moiety, along with a second positive potential wave at +1.95 V vs. Fc/Fc⁺ due to the oxidation of the thienyl group. The irreversible reduction of the metal centre is observed at -0.89 V vs. Fc/Fc⁺. Subsequent cycles indicate that decomposition of the complex occurs, with new peaks at +0.13 V in the anodic direction and +0.55 V, -0.12 V and -0.74 V vs. Fc/Fc⁺ in the cathodic direction being produced. A reduction in the intensity of the reductive peak at -0.74 V relative to the reduction of the cobalt unit (-0.89 V) was observed compared for this system. This would suggest that while decomposition of the complex is occurring, deposition onto the electrodes is not.

![Cyclic voltammogram of NB-C6 showing oxidation and reduction waves.](image)

*Figure B5*  
Cyclic voltammogram of **NB-C6** showing oxidation and reduction waves.
In NB-L7, the CV displays one irreversible oxidation and one irreversible reduction (Fig. B6). The oxidation due to the thienyl group occurs at $E_{pa} = +1.90$ V vs. Fc/Fc$^+$. This is higher than that of the previous thiophene based oxidations and is due to the electron withdrawing nature of the dicyanovinyl moiety attached at the 5’ position of the thiophene group. The dicyanovinyl unit itself is reduced irreversibly at $E_{pc} = -0.98$ V vs. Fc/Fc$^+$. This value corresponds well with published results where the irreversible reduction of a dicyanovinyl moiety attached to an aryl group is reduced at approximately 1 V.\textsuperscript{7}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{cyclic_voltamogram_nb_l7.png}
\caption{Cyclic voltammogram of NB-L7 showing oxidation and reduction waves.}
\end{figure}
For **NB-L8**, the irreversible oxidation of the thienyl group was observed at +1.39 V vs. Fc/Fc⁺ (Fig. B7, a). Two further oxidations were observed at higher potentials, +1.66 and +1.99 V vs. Fc/Fc⁺. These are tentatively assigned to the oxidation of the phenanthrene moiety. Potential cycling over the peak potential produced a deposition on the electrodes and the redox response became progressively distorted. Also a new reductive peak at -0.12 V vs. Fc/Fc⁺ was observed which may indicate that decomposition was occurring. The disubstituted dicobalt complex **NB-C8** gave results analogous to the other dicobalt carbonyl complexes discussed above. Two anodic waves were observed at potentials of +0.91 V and +1.39 V vs. Fc/Fc⁺ which are attributed to irreversible oxidations on the metal centre and thiophene unit (Fig. B7, b). No other oxidation processes were observed out to the solvent limit. Reductive cycling produced an irreversible cathodic wave at -0.95 V vs. Fc/Fc⁺ which is due to the formation of the radical anion. Successive redox cycles produced a new anodic wave at +0.16 followed by a cathodic wave at -0.66V vs. Fc/Fc⁺. The former oxidation is ascribed to the degradation of the radical anion produced by the initial reductive process while the latter reductive wave corresponds well to the reduction of chemically adsorbed cobalt containing products on the electrode.
Figure B7  Cyclic voltammogram of NB-L8 (a) and NB-C8 (b) showing oxidation and reduction waves.
Photolysis of NB-C2 at $\lambda_{\text{exc}} > 520$ nm for 30 minutes resulted in bleaching of the parent absorbance bands at 2090, 2055 and 2028 cm$^{-1}$ and generation of weak product bands at 2064, 2018 and 2005 cm$^{-1}$ assigned to formation of the pentacarbonyl species NB-C2-Co$_2$(CO)$_5$(PPh$_3$) (Fig. C1). Subsequent photolysis at $\lambda_{\text{exc}} > 410$ nm for 12 minutes resulted in a substantial increase in the intensity of these bands along with the appearance of new bands at 1996, 1980 and 1971 cm$^{-1}$ which were tentatively assigned to the disubstituted species, NB-C2-Co$_2$(CO)$_4$(PPh$_3$)$_2$. Continued irradiation of the sample at $\lambda_{\text{exc}} > 320$ nm (5 minutes) resulted in minimal growth of the pentacarbonyl product bands and substantial growth of the tetracarbonyl species. The product bands compared favourably with those observed by Coleman et al.$^9$ and Arnanz et al.$^{3,4}$

**Figure C1** Infrared difference spectra following irradiation of NB-C2 in hexane with PPh$_3$ at $\lambda_{\text{exc}} > 520$ nm (black lines, 30 minutes total irradiation), $\lambda_{\text{exc}} > 410$ nm (red lines, 12 minutes total irradiation) and $\lambda_{\text{exc}} > 320$ nm (blue lines, 5 minutes total irradiation). Negative bands indicate bleaching of the parent complex while positive bands indicate generation of the PPh$_3$ trapped photoproducts.
Irradiation of **NB-C3** in hexane solution in the presence of triphenylphosphine at \( \lambda_{\text{exc}} > 520 \) nm for 30 minutes resulted in the depletion of the parent bands at 2091, 2058 and 2031 cm\(^{-1}\) with concomitant generation of positive bands at 2065, 2020 and 2007 cm\(^{-1}\) (Fig. C2) that correspond to the trapped monosubstituted triphenylphosphine species, **NB-C3-Co\(_2\)(CO)\(_5\)(PPh\(_3\))**. Irradiation at \( \lambda_{\text{exc}} > 410 \) nm for 10 minutes resulted in intensification of the product bands and the appearance bands due to the tetracarbonyl photoproduct at 1984 and 1973 cm\(^{-1}\). Irradiation at \( \lambda_{\text{exc}} > 320 \) nm (5 minutes) resulted predominantly in the growth of the tetracarbonyl bands. Two additional weak bands were observed at 1951 and 1941 cm\(^{-1}\) which were also attributed to the tetracarbonyl species, **NB-C3-Co\(_2\)(CO)\(_4\)(PPh\(_3\))\(_2\)**. Product assignment was based on matching of IR bands with those in literature.\(^{4,9}\)

**Figure C2**  Infrared difference spectra following irradiation of **NB-C3** in hexane with PPh\(_3\) at \( \lambda_{\text{exc}} > 520 \) nm (black lines, 30 minutes total irradiation), \( \lambda_{\text{exc}} > 410 \) nm (red lines, 10 minutes total irradiation) and \( \lambda_{\text{exc}} > 320 \) nm (blue lines, 5 minutes total irradiation). Negative bands indicate bleaching of the parent complex while positive bands indicate generation of the pentacarbonyl and tetracarbonyl species.
C3  Steady state photolysis of NB-C4

Under similar conditions ($\lambda_{\text{exc}} > 520$ nm for 30 minutes, $\lambda_{\text{exc}} > 410$ nm for 22 minutes and $\lambda_{\text{exc}} > 320$ nm for 5 minutes) NB-C4 resulted in bleaching of the parent absorbance bands at 2091, 2082, 2059 and 2032 cm$^{-1}$ and generation of bands at 2065, 2019 and 2007 cm$^{-1}$ which were assigned to the pentacarbonyl species, NB-C4-Co$_2$(CO)$_5$(PPh$_3$) and bands at 1997, 1972 and 1943 cm$^{-1}$ that were assigned to NB-C4-Co$_2$(CO)$_4$(PPh$_3$)$_2$ (Fig. C3). These product bands are similar to those observed by Long et al. and Arnanz et al.

Figure C3  Infrared difference spectra following irradiation of NB-C4 in hexane with PPh$_3$ at $\lambda_{\text{exc}} > 520$ nm (black lines, 30 minutes total irradiation), $\lambda_{\text{exc}} > 410$ nm (red lines, 22 minutes total irradiation) and $\lambda_{\text{exc}} > 320$ nm (blue lines, 5 minutes total irradiation). Negative bands indicate bleaching of the parent complex while positive bands indicate generation of the pentacarboxyl and tetracarboxyl species.
Irradiation of the dicobalt hexacarbonyl complex, NB-C5, in hexane solution with trapping ligand (PPh$_3$) at $\lambda_{\text{exc}} > 520$ nm for 30 minutes resulted in the depletion of parent bands at 2092, 2057, 2030 cm$^{-1}$ and the generation of weak product bands at 2065, 2019 and 2007 cm$^{-1}$ that were assigned to the pentacarbonyl photoprodut NB-C5-Co$_2$(CO)$_5$(PPh$_3$) (Fig. C4). Further photolysis at $\lambda_{\text{exc}} > 410$ nm for 20 minutes caused intensification of the pentacarbonyl bands and generated bands at 1997 and 1972 cm$^{-1}$ while 5 minutes photolysis at $\lambda_{\text{exc}} > 320$ nm produced a weak band at 1943 cm$^{-1}$. By comparison with the results obtained by Long et al.$^8$ these new absorbance bands are indicative of formation of the triphenylphosphine trapped pentacarbonyl species, and by comparison with results obtained by Arnanz et al subsequent formation of the tetracarbonyl species.$^4$

*Figure 41*  Infrared difference spectra following irradiation of NB-C5 in hexane with PPh$_3$ at $\lambda_{\text{exc}} > 520$ nm (black lines, 30 minutes total irradiation), $\lambda_{\text{exc}} > 410$ nm (red lines, 20 minutes total irradiation) and $\lambda_{\text{exc}} > 320$ nm (blue lines, 5 minutes total irradiation). Negative bands indicate bleaching of the parent complex while positive bands indicate generation of the pentacarbonyl and tetracarbonyl species.
When the dicobalt hexacarbonyl complex, **NB-C7**, was photolysed under the analogous conditions ($\lambda_{exc} > 520$ nm, $\lambda_{exc} > 410$ nm and $\lambda_{exc} > 320$ nm) similar processes were observed. Depletion of parent bands at 2094, 2061 and 2034 cm$^{-1}$ occurred together with the generation of weak new pentacarbonyl product bands at 2067, 2021 and 2009 cm$^{-1}$ assigned to **NB-C7-Co$_2$(CO)$_5$(PPh$_3$)** following irradiation at $\lambda_{exc} > 520$ nm for 30 minutes (Fig. C5). Higher energy broadband irradiation ($\lambda_{exc} > 410$ nm for 10 minutes) increased the rate of pentacarbonyl product formation signified by growth of the bands at 2067, 2021 and 2009 cm$^{-1}$ with the concomitant generation of a new band at 1974 cm$^{-1}$. The new band increased in intensity following irradiation at $\lambda_{exc} > 320$ nm (5 minutes) with growth of a further weak band at 1960 cm$^{-1}$ confirming the formation of the tetracarbonyl species, **NB-C7-Co$_2$(CO)$_4$(PPh$_3$)$_2$**. All bands observed agree well with those reported for other dicobalt pentacarbonyl and tetracarbonyl complexes.$^{4,8,9}$

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**Figure C5**  
Infrared difference spectra following irradiation of **NB-C7** in hexane with PPh$_3$ at $\lambda_{exc} > 520$ nm (black lines, 30 minutes total irradiation), $\lambda_{exc} > 410$ nm (red lines, 10 minutes total irradiation) and $\lambda_{exc} > 320$ nm (blue lines, 5 minutes total irradiation). Negative bands indicate bleaching of the parent complex while positive bands indicate generation of the pentacarbonyl and tetracarbonyl species.
Ethynylferrocene was synthesised according to the method outlined by Coleman et al.\textsuperscript{9} HLPC grade, nitrogen purged hexane was charged with ethynylferrocene (0.95 mmol / 200 mg) and Co\textsubscript{2}(CO)\textsubscript{8} (0.95 mmol / 320 mg). The solution was allowed to stir for 18 hours under an inert atmosphere in the dark. The solvent was removed \textit{via} rotary evaporation resulting in a dark residue. The crude product was purified by column chromatography on silica gel using hexane : CH\textsubscript{2}Cl\textsubscript{2} 70 : 30 as mobile phase affording a dark green solid. Yield: 210 mg, 0.42 mmol, 44 %. 

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): 6.28 (1H, s), 4.35 (2H, s), 4.33 (2H, s), 4.16 (5H, s) ppm. IR (CH\textsubscript{2}Cl\textsubscript{2}): \(\nu(\text{CO})\) 2093, 2054, 2032, 2022, 2210 cm\(^{-1}\).
Synthesis of diphenylacetylene dicobalt pentacarbonyl triphenylphosphine, PhCCPh-Co\(_2\)(CO)\(_5\)(PPh\(_3\))

Diphenylacetylene dicobalt pentacarbonyl triphenylphosphine was prepared by a thermal substitution reaction. Diphenylacetylene dicobalt hexacarbonyl was dissolved in hexane (25 ml) and purged with nitrogen for 5 minutes. A molar excess of triphenylphosphine was added and the solution was heated to 50 ºC. The progress of the reaction was monitored by TLC. The diphenylacetylene dicobalt hexacarbonyl, pentacarbonyl and tetracarbonyl complexes possess R\(_f\) values on silica [petroleum ether : CH\(_2\)Cl\(_2\) (3 : 1)] of 0.73, 0.50 and 0.17 respectively. The reaction mixture was cooled and the solvent removed when the tetracarbonyl species was first observed by TLC. The crude reaction mixture was purified by column chromatography on silica gel using petroleum ether : CH\(_2\)Cl\(_2\) (3 : 1) as mobile phase which afforded the pure pentacarbonyl product as a brown solid.

\(^1\)H NMR (400 MHz, CDCl\(_3\)): 7.60-7.56 (10H, m), 7.47-7.43 (15H, m) ppm. IR (hexane): v(CO) 2062, 2016, 2005 cm\(^{-1}\)
Synthesis of 2-(phenylethynyl)thiophene dicobalt pentacarbonyl triphenylphosphine, ThCCPh-Co$_2$(CO)$_5$(PPh$_3$)

2-(Phenylethynyl)thiophene dicobalt pentacarbonyl triphenylphosphine was prepared by a thermal substitution reaction. 2-(Phenylethynyl)thiophene dicobalt hexacarbonyl was dissolved in hexane (25 ml) and purged with nitrogen for 5 minutes. A molar excess of triphenylphosphine was added and the solution was heated to 75 °C. The progress of the reaction was monitored by TLC. The R$_f$ values of the hexacarbonyl, pentacarbonyl and tetracarbonyl complexes possess R$_f$ values on silica [petroleum ether : CH$_2$Cl$_2$ (3 : 1)] of 0.77, 0.42 and 0.13 respectively. The reaction mixture was cooled and the solvent removed when the tetracarbonyl species was first observed by TLC. The crude reaction mixture was purified by column chromatography on silica gel using petroleum ether : CH$_2$Cl$_2$ (3 : 1) as mobile phase which afforded the pure pentacarbonyl product as a brown solid.

$^1$H NMR (400 MHz, CDCl$_3$): 7.57-7.52 (8H, m), 7.50-7.34 (10H, m) 7.32-7.25 (5H, m) ppm. IR (hexane): ν(CO) 2063, 2021, 2005 cm$^{-1}$
Ethynylferrocene dicobalt pentacarbonyl triphenylphosphine was prepared by a thermal substitution reaction. Ethynylferrocene dicobalt hexacarbonyl was dissolved in hexane (25 ml) and purged with nitrogen for 5 minutes. A molar excess of triphenylphosphine was added and the solution was heated to 50 °C. The progress of the reaction was monitored by TLC. The Rf values of the respective ethynl dicobalt hexacarbonyl, pentacarbonyl and tetracarbonyl complexes possess Rf values on silica [petroleum ether : CH2Cl2 (3 : 1)] of 0.75, 0.43 and 0.18 respectively. The reaction mixture was cooled and the solvent removed when the tetracarbonyl species was first observed by TLC. The crude reaction mixture was purified by column chromatography on silica gel using petroleum ether : CH2Cl2 (3 : 1) as mobile phase which afforded the pure pentacarbonyl product as a dark green solid.

\(^1\text{H NMR}\) (400 MHz, CDCl3): 7.52-7.40 (9H, m), 7.11-7.04 (6H, m), 6.06 -6.04 (1H, m), 4.38 (2H, s), 4.22 (2H, s), 4.03 (5H, s) ppm. \(\text{IR (hexane): } \nu(\text{CO})\) 2063, 2012, 2004 cm\(^{-1}\)
**F1 Quantum yield method**

All quantum yields were carried out using a liquid-phase potassium ferrioxalate actinometer. The actinometer was prepared by mixing three volumes of 1.5 M K$_2$C$_2$O$_4$ solution with one volume of 1.5 M FeCl$_3$ solution with agitation. The precipitated K$_3$Fe(C$_2$O$_4$)$_3$.3H$_2$O was then recrystallised three times from warm water and dried in a current of warm air. To prepare 1 L of 0.006 M K$_3$Fe(C$_2$O$_4$)$_3$.3H$_2$O solution, 2.947 g of the precipitate was dissolved in 800 ml water, 100 ml 1.0 N sulphuric acid was added and filled to the mark with water. While the 0.15 M actinometric solution required 73.68 g of precipitate to be added to the same volumes of liquid. For all quantitative work the preparation and manipulation of the ferrioxalate solutions must be carried out in a darkroom, using a red photographic safelight. The light intensity in a photochemical reaction is determined by irradiating ferrioxalate solution and monitoring the subsequent change in absorbance at 510 nm. A carousel was used to house both the actinometer and sample cells so that they were equally exposed to a uniform amount of irradiation during each experiment. The carousel operated inside a black box to prevent any stray light reaching the sample or actinometer solutions. An autopipette was to ensure all volumes were accurately measured.

For each actinometric measurement a quartz cuvette was charged with 3 ml ($V_1$) of ferrioxalate solution. The cell was placed in the carousel and irradiated. After the determined irradiation time ($t$), the solution was well mixed and an aliquot volume (2 ml, $V_2$) was pipette into a volumetric flask (10 ml, $V_3$). Buffer solution of volume equal to half the volume of photolyte placed in the flask was added (1 ml), so too was 2 ml phenanthroline solution (0.1 g per cent by weight solution). The solution was diluted with distilled water to the $V_3$ volume mark and mixed well. The flask was wrapped in tinfoil and the solution allowed to develop. After one hour, the absorbance of the solution was measured in a 1cm cell at 510 nm in spectrophotometer using a blank iron free solution as a reference.
The number of Fe$^{2+}$ ions ($n_{Fe^{2+}}$) formed during photolysis can be calculated from:

$$n_{Fe^{2+}} = \frac{6.023 \times 10^{20} V_1 V_3 \log_{10} (I_0/I)}{V_2 l \varepsilon}$$

where

- $V_1$ = Volume of actinometer solution irradiated (ml)
- $V_2$ = Volume of aliquot taken for analysis (ml)
- $V_3$ = Final volume to which the aliquot $V_2$ is diluted (ml)
- $\log_{10} (I_0/I)$ = measured optical density of the solution
- $l$ = path length of the spectrophotometer cell used (cm)
- $\varepsilon$ = experimental value of the molar extinction coefficient of Fe$^{2+}$ complex, determined from the slope of the calibration plot (approx. equal to $1.11 \times 10^4$ l mol$^{-1}$ cm$^{-1}$).

The number of quanta absorbed by the actinometer ($n_a$) per second is obtained from

$$n_a = n_{Fe^{2+}} / \Phi_\lambda t$$

where $t$ is the time in seconds.

For each sample under investigation, a solution of known concentration was prepared so that the optical density of each was $0.8 \pm 0.1$ AU at 400 nm. A 10% excess of triphenyl phosphine was used as a trapping ligand throughout the measurements and added to each solution immediately prior to irradiation. Each sample cuvette was accurately charged with 3 ml of the alkynyl dicobalthexacarbonyl / triphenylphosphine solution. The sample cell was placed in the carousel with the actinometric solutions and were irradiated in parallel. The change in absorbance of the sample solution was measured at 400 nm to calculate the yield of CO loss that occurred.
Extinction coefficients of dicobalt hexacarbonyl complexes and corresponding pentacarbonyl complexes recorded in cyclohexane.

<table>
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<tr>
<th>Hexacarbonyl Complex</th>
<th>$\varepsilon$ (M$^{-1}$ cm$^{-1}$) at 400 nm</th>
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<tbody>
<tr>
<td>PhCCPh-Co$_2$(CO)$_6$</td>
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</tr>
<tr>
<td>ThCCPh-Co$_2$(CO)$_6$</td>
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<td>FeCCH-Co$_2$(CO)$_6$</td>
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<table>
<thead>
<tr>
<th>Photolytic/thermal substitution products</th>
<th>$\varepsilon$ (M$^{-1}$ cm$^{-1}$) at 400 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>PhCCPh-Co$_2$(CO)$_5$PPh$_3$</td>
<td>8179</td>
</tr>
<tr>
<td>ThCCPh-Co$_2$(CO)$_5$PPh$_3$</td>
<td>4680</td>
</tr>
<tr>
<td>FeCCH-Co$_2$(CO)$_5$PPh$_3$</td>
<td>2717</td>
</tr>
</tbody>
</table>
F2 Quantum yield calculations

(a) Quantum yield determinations of CO loss for $[(\mu_2\text{-PhCCPh})\text{-Co}_2(\text{CO})_6] \ (1)$

Molar excitation coefficients at 400 nm

$\begin{align*}
(\mu_2\text{-PhCCPh})\text{-Co}_2(\text{CO})_6 \ (1) & \quad 1,140 \text{ M}^{-1} \text{ cm}^{-1} \\
(\mu_2\text{-PhCCPh})\text{-Co}_2(\text{CO})_5(\text{PPh}_3) & \quad 8,179 \text{ M}^{-1} \text{ cm}^{-1}
\end{align*}$

Irradiation of $1$ at 313 nm (21 mins)

Increase in intensity of band at 400 nm = 0.16
Molar increase = $2.34 \times 10^{-5}$ molar
Moles converted per second = $1.9 \times 10^{-8}$ moles/s
For a 3 cm$^3$ sample, number of molecules photolysed per second = $3.35 \times 10^{13}$ molecules/s

Change in absorbance of actinometer solution at 510 nm
Absorbance at 510 nm = 0.823
Number of Fe$^{2+}$ ions = $6.70 \times 10^{17}$ ions
Using a quantum yield for Fe$^{2+}$ production of 1.24 at 313 nm
Number of photons emitted by the source at 313 nm = $5.40 \times 10^{17}$
Number of photons emitted per second by the source at 313 nm = $4.29 \times 10^{14}$ photons/s
Number of photons absorbed by the sample = $4.29 \times 10^{14}$ photons/s
Quantum yield of photochemical reaction is $(3.35 \times 10^{13}) / (4.29 \times 10^{14}) = 0.078$

Irradiation of $1$ at 365 nm (20 mins)

Increase in intensity of band at 400 nm = 0.15
Molar increase = $2.19 \times 10^{-5}$ molar
Moles converted per second = $1.8 \times 10^{-8}$ moles/s
For a 3 cm$^3$ sample, number of molecules photolysed per second = $3.30 \times 10^{13}$ molecules/s

Change in absorbance of actinometer solution at 510 nm
Absorbance at 510 nm = 1.70
Number of Fe$^{2+}$ ions = $1.39 \times 10^{18}$ ions
Using a quantum yield for Fe$^{2+}$ production of 1.21 at 365 nm
Number of photons emitted by the source at 365 nm = $5.40 \times 10^{17}$
Number of photons emitted per second by the source at 313 nm = $9.56 \times 10^{14}$ photons/s
Number of photons absorbed by the sample = $9.56 \times 10^{14}$ photons/s
Quantum yield of photochemical reaction is $(3.30 \times 10^{13}) / (9.56 \times 10^{14}) = 0.035$

**Irradiation of 1 at 405 nm (15 mins)**
Increase in intensity of band at 400 nm = 0.074
Molar increase = $1.09 \times 10^{-5}$ molar
Moles converted per second = $1.2 \times 10^{-8}$ moles/s
For a 3 cm$^3$ sample, number of molecules photolysed per second = $2.19 \times 10^{13}$ molecules/s

**Change in absorbance of actinometer solution at 510 nm**
Absorbance at 510 nm = 1.02
Number of Fe$^{2+}$ ions = $8.31 \times 10^{17}$ ions
Using a quantum yield for Fe$^{2+}$ production of 1.14 at 405 nm
Number of photons emitted by the source at 405 nm = $7.29 \times 10^{17}$
Number of photons emitted per second by the source at 405 nm = $8.10 \times 10^{14}$ photons/s
Number of photons absorbed by the sample = $8.10 \times 10^{14}$ photons/s
Quantum yield of photochemical reaction is $(2.19 \times 10^{13}) / (8.10 \times 10^{14}) = 0.027$

**Irradiation of 1 at 546 nm (60 mins)**
Increase in intensity of band at 400 nm = 0.114
Molar increase = $1.69 \times 10^{-5}$ molar
Moles converted per second = $5.0 \times 10^{-9}$ moles/s
For a 3 cm$^3$ sample, number of molecules photolysed per second = $8.47 \times 10^{12}$ molecules/s

**Change in absorbance of actinometer solution at 510 nm**
Absorbance at 510 nm = 0.123
Number of Fe$^{2+}$ ions = $1.00 \times 10^{17}$ ions
Using a quantum yield for Fe$^{2+}$ production of 0.15 at 546 nm
Number of photons emitted by the source at 546 nm = $6.68 \times 10^{17}$
Number of photons emitted per second by the source at 546 nm = $1.87 \times 10^{14}$ photons/s
Number of photons absorbed by the sample = $1.87 \times 10^{14}$ photons/s
Quantum yield of photochemical reaction is $(8.47 \times 10^{12}) / (1.87 \times 10^{14}) = 0.045$

(b) Quantum yield determinations of $[(\mu_2'-\text{ThCCPh})-\text{Co}_2(\text{CO})_6]$ (2)

Molar excitation coefficients at 400 nm
$[(\mu_2'-\text{PhCCPh})-\text{Co}_2(\text{CO})_6]$ (2) $2,314 \text{ M}^{-1} \text{ cm}^{-1}$
$[(\mu_2'-\text{PhCCPh})-\text{Co}_2(\text{CO})_5(\text{PPh}_3)]$ $4,829 \text{ M}^{-1} \text{ cm}^{-1}$

Irradiation of 2 at 313 nm (10 mins)
Increase in intensity of band at 400 nm = 0.077
Molar increase = $3.07 \times 10^{-5}$ molar
Moles converted per second = $5.1 \times 10^{-8}$ moles/s
For a 3 cm$^3$ sample, number of molecules photolysed per second = $9.21 \times 10^{13}$ molecules/s

Change in absorbance of actinometer solution at 510 nm
Absorbance at 510 nm = 0.5862
Number of Fe$^{2+}$ ions = $4.77 \times 10^{17}$ ions
Using a quantum yield for Fe$^{2+}$ production of 1.24 at 313 nm
Number of photons emitted by the source at 313 nm = $3.85 \times 10^{17}$
Number of photons emitted per second by the source at 313 nm = $6.41 \times 10^{14}$ photons/s
Number of photons absorbed by the sample = $6.41 \times 10^{14}$ photons/s
Quantum yield of photochemical reaction is $(9.21 \times 10^{13}) / (6.41 \times 10^{14}) = 0.145$

Irradiation of 2 at 365 nm (15 min)
Increase in intensity of band at 400 nm = 0.099
Molar increase = $3.94 \times 10^{-5}$ molar
Moles converted per second = $4.4 \times 10^{-8}$ moles/s
For a 3 cm$^3$ sample, number of molecules photolysed per second = $7.91 \times 10^{13}$ molecules/s
Change in absorbance of actinometer solution at 510 nm
Absorbance at 510 nm = 1.3191
Number of Fe$^{2+}$ ions = 1.07 x 10$^{18}$ ions
Using a quantum yield for Fe$^{2+}$ production of 1.21 at 365 nm
Number of photons emitted by the source at 365 nm = 8.87 x 10$^{17}$
Number of photons emitted per second by the source at 313 nm = 9.85 x 10$^{14}$ photons/s
Number of photons absorbed by the sample = 9.85 x 10$^{14}$ photons/s
Quantum yield of photochemical reaction is (7.91 x 10$^{13}$) / (9.85 x 10$^{14}$) = 0.0803

Irradiation of 2 at 405 nm (15 mins)
Increase in intensity of band at 400 nm = 0.046
Molar increase = 1.83 x 10$^{-5}$ molar
Moles converted per second = 2.0 x 10$^{-8}$ moles/s
For a 3 cm$^3$ sample, number of molecules photolysed per second = 3.67 x 10$^{13}$ molecules/s

Change in absorbance of actinometer solution at 510 nm
Absorbance at 510 nm = 1.02
Number of Fe$^{2+}$ ions = 8.31 x 10$^{17}$ ions
Using a quantum yield for Fe$^{2+}$ production of 1.14 at 405 nm
Number of photons emitted by the source at 405 nm = 7.29 x 10$^{17}$
Number of photons emitted per second by the source at 405 nm = 8.10 x 10$^{14}$ photons/s
Number of photons absorbed by the sample = 8.10 x 10$^{14}$ photons/s
Quantum yield of photochemical reaction is (3.67 x 10$^{13}$) / (8.10 x 10$^{14}$) = 0.045

Irradiation of 2 at 546 nm (40 mins)
Increase in intensity of band at 400 nm = 0.073
Molar increase = 2.91 x 10$^{-5}$ molar
Moles converted per second = 1.2 x 10$^{-9}$ moles/s
For a 3 cm$^3$ sample, number of molecules photolysed per second = 2.19 x 10$^{13}$ molecules/s

Change in absorbance of actinometer solution at 510 nm
Absorbance at 510 nm = 0.0907
Number of Fe\(^{2+}\) ions = 7.38 x 10\(^{16}\) ions
Using a quantum yield for Fe\(^{2+}\) production of 0.15 at 546 nm
Number of photons emitted by the source at 546 nm = 4.92 x 10\(^{17}\)
Number of photons emitted per second by the source at 546 nm = 2.05 x 10\(^{14}\) photons/s
Number of photons absorbed by the sample = 2.05 x 10\(^{14}\) photons/s
Quantum yield of photochemical reaction is \((2.19 \times 10^{13}) / (2.05 \times 10^{14}) = 0.106\)

(c) Quantum yield determinations of \([((\mu_2\text{-FcCCH})\text{-Co}_2\text{(CO)})_6]\) (3)

Molar excitation coefficients at 400 nm
\((\mu_2\text{-FcCCH})\text{-Co}_2\text{(CO)}_6\) (3) \(1,497 \text{ M}^{-1} \text{ cm}^{-1}\)
\((\mu_2\text{-FcCCH})\text{-Co}_2\text{(CO)}_5\text{(PPh}_3\text{)}\) \(2,717 \text{ L mol}^{-1} \text{ cm}^{-1}\)

Irradiation of 3 at 313 nm (20 mins)
Increase in intensity of band at 400 nm = 0.072
Molar increase = \(1.21 \times 10^{-4}\) molar
Moles converted per second = \(1.0 \times 10^{-7}\) moles/s
For a 3 cm\(^3\) sample, number of molecules photolysed per second = \(1.81 \times 10^{14}\) molecules/s

Change in absorbance of actinometer solution at 510 nm
Absorbance at 510 nm = 1.2258
Number of Fe\(^{2+}\) ions = 9.98 x 10\(^{17}\) ions
Using a quantum yield for Fe\(^{2+}\) production of 1.24 at 313 nm
Number of photons emitted by the source at 313 nm = 8.04 x 10\(^{17}\)
Number of photons emitted per second by the source at 313 nm = 6.71 x 10\(^{14}\) photons/s
Number of photons absorbed by the sample = 6.71 x 10\(^{14}\) photons/s
Quantum yield of photochemical reaction is \((1.81 \times 10^{14}) / (6.71 \times 10^{14}) = 0.269\)

Irradiation of 3 at 365 nm (25 mins)
Increase in intensity of band at 400 nm = 0.084
Molar increase = \(6.68 \times 10^{-5}\) molar
Moles converted per second = \(4.6 \times 10^{-8}\) moles/s 
For a 3 cm\(^3\) sample, number of molecules photolysed per second = \(8.26 \times 10^{13}\) molecules/s

*Change in absorbance of actinometer solution at 510 nm*

Absorbance at 510 nm = 1.993 
Number of Fe\(^{2+}\) ions = \(1.62 \times 10^{18}\) ions 
Using a quantum yield for Fe\(^{2+}\) production of 1.21 at 365 nm 
Number of photons emitted by the source at 365 nm = \(1.34 \times 10^{18}\) 
Number of photons emitted per second by the source at 365 nm = \(1.16 \times 10^{15}\) photons/s 
Number of photons absorbed by the sample = \(1.16 \times 10^{15}\) photons/s 
Quantum yield of photochemical reaction is \((8.26 \times 10^{13}) / (1.16 \times 10^{15}) = 0.071\)

*Irradiation of 3 at 405 nm (25 mins)*

Increase in intensity of band at 400 nm = 0.044 
Molar increase = \(3.61 \times 10^{-5}\) molar 
Moles converted per second = \(2.4 \times 10^{-8}\) moles/s 
For a 3 cm\(^3\) sample, number of molecules photolysed per second = \(4.35 \times 10^{13}\) molecules/s

*Change in absorbance of actinometer solution at 510 nm*

Absorbance at 510 nm = 1.952 
Number of Fe\(^{2+}\) ions = \(1.59 \times 10^{18}\) ions 
Using a quantum yield for Fe\(^{2+}\) production of 1.14 at 405 nm 
Number of photons emitted by the source at 405 nm = \(1.39 \times 10^{18}\) 
Number of photons emitted per second by the source at 405 nm = \(9.30 \times 10^{14}\) photons/s 
Number of photons absorbed by the sample = \(9.30 \times 10^{14}\) photons/s 
Quantum yield of photochemical reaction is \((4.35 \times 10^{13}) / (9.30 \times 10^{14}) = 0.047\)

*Irradiation of 3 at 546 nm (35 mins)*

Increase in intensity of band at 400 nm = 0.133 
Molar increase = \(5.27 \times 10^{-5}\) molar 
Moles converted per second = \(2.5 \times 10^{-8}\) moles/s 
For a 3 cm\(^3\) sample, number of molecules photolysed per second = \(4.54 \times 10^{13}\) molecules/s
Change in absorbance of actinometer solution at 510 nm

Absorbance at 510 nm = 0.075

Number of Fe\(^{2+}\) ions = 6.14 x 10\(^{16}\) ions

Using a quantum yield for Fe\(^{2+}\) production of 0.15 at 546 nm

Number of photons emitted by the source at 546 nm = 4.09 x 10\(^{17}\)

Number of photons emitted per second by the source at 546 nm = 1.95 x 10\(^{14}\) photons/s

Number of photons absorbed by the sample = 4.09 x 10\(^{14}\) photons/s

Quantum yield of photochemical reaction is (4.54 x 10\(^{13}\)) / (1.95 x 10\(^{14}\)) = 0.233
TRIR difference spectra at 7, 20, 50, 100 and 200 ps following excitation of PhCCPh-Co₂(CO)₆ in CH₃CN at 400 nm.
TRIR difference spectra at 10, 25, 50, 100 250 and 500 ps following excitation of PhCCPh-Co$_2$(CO)$_6$ in pentane at 400 nm.
TRIR of FeCCH-Co$_2$(CO)$_6$ in CH$_3$CN

TRIR difference spectra at 10, 25, 50, 100 and 250 ps following excitation of FeCCH-Co$_2$(CO)$_6$ in CH$_3$CN at 400 nm.
TRIR difference spectra at 10, 25, 50, 100, 250 and 1000 ps following excitation of FeCCH-Co$_2$(CO)$_6$ in THF at 532 nm with PPh$_3$ as trapping ligand.
Steady state photolysis of \( \text{FcCCH-Co}_2(\text{CO})_6 \)

Extended monochromatic photolysis of the dicobalt hexacarbonyl complex, \( \text{FcCCH-Co}_2(\text{CO})_6 \), in hexane solution in the presence of triphenylphosphine at \( \lambda_{\text{exc}} = 546 \) nm for 30 minutes caused minor changes in the IR spectrum. Bleaching of the parent IR bands at 2093, 2054, 2032 and 2022 cm\(^{-1}\) with concomitant generation of weak product bands at 2063, 2012, and 2004 cm\(^{-1}\) was observed and assigned to the generation of the pentacarbonyl photoproduct, \( \text{FcCCH-Co}_2(\text{CO})_5(\text{PPh}_3) \). These IR bands continued to grow following irradiation at \( \lambda_{\text{exc}} = 436 \) nm for 20 minutes with the generation of a further bands at 1992, 1974 and 1941 cm\(^{-1}\) which were attributed to the tetracarbonyl species, \( \text{FcCCH-Co}_2(\text{CO})_4(\text{PPh}_3)_2 \). Subsequent photolysis at \( \lambda_{\text{exc}} = 313 \) nm for 20 minutes resulted in a notable increase in the intensity of the pentacarbonyl and tetracarbonyl photoproducts. The assignment of bands to the pentacarbonyl species, \( \text{FcCCH-Co}_2(\text{CO})_5(\text{PPh}_3) \), was based on IR bands of isolated \( \text{FcCCH-Co}_2(\text{CO})_5(\text{PPh}_3) \) complex while the assignment of the tetracarbonyl species were based on similarities with isolated tetracarbonyl complexes.\(^{10}\)

\[ \text{Infrared difference spectra following monochromatic irradiation of } \text{FcCCH-Co}_2(\text{CO})_6 \text{ in hexane with PPh}_3 \text{ at } \lambda_{\text{exc}} = 546 \text{ nm (black lines, 20 minutes total irradiation), } \lambda_{\text{exc}} = 436 \text{ nm (red lines, 30 minutes total irradiation time) and } \lambda_{\text{exc}} = 313 \text{ nm (blue lines, 30 minutes total irradiation time). Negative bands indicate bleaching of the parent complex while positive bands indicate generation of the pentacarbonyl species.} \]
I Theoretical calculations

All theoretical calculations were carried out by Prof. C. Long, at Dublin City University.

Initial coordinates for the structural optimization of \((\mu_2-C_2H_2)Co_2(CO)_6\) were obtained from Platts et al.\(^{11}\) The B3LYP/LANL2DZp model chemistry was used for all the calculations as implemented in Gaussian03.\(^{12}\)

The Hessian matrix was calculated to predict the infrared spectrum of \((\mu_2-C_2H_2)Co_2(CO)_6\). The predicted \(\nu(CO)\) bands of this complex were corrected by comparison with the published IR spectrum.\(^{13}\) This yielded a correction factor of 1.0222 which was then used to correct the calculated \(\nu(CO)\) bands of the equivalent ground state triplet species.

<table>
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<tr>
<th>(\nu(CO)) (cm(^{-1}))</th>
<th>Observed</th>
<th>2097.8</th>
<th>2058.5</th>
<th>2033.7</th>
<th>2028.1</th>
<th>2016.6</th>
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<tr>
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<td>2097.9</td>
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<td>2012.7</td>
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<tr>
<td>Triplet</td>
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<td>2021.7</td>
<td>2015.2</td>
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<td>(\Delta \nu)</td>
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<td>6.3</td>
<td>1.4</td>
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*Table 1* Observed spectrum and calculated singlet and triplet state spectra for \((\mu_2-C_2H_2)Co_2(CO)_6\)
### Mulliken atomic spin densities:

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<td>18</td>
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Sum of Mulliken spin densities = 2.00000

*Table 2*  
*Mulliken atomic spin densities: for* $^3\{\mu_2\text{-C}_2\text{H}_2\}\text{Co}_2\text{(CO)}_6$ *at B3LYP/LANL2DZp*
**TD DFT Results for Singlet to Singlet transitions** in \((\mu_2-C_2H_2)Co_2(CO)_6\)

Excitation energies and oscillator strengths:

<table>
<thead>
<tr>
<th>Excited State 1: Singlet-B1</th>
<th>2.1748 eV</th>
<th>570.09 nm</th>
<th>f=0.0013</th>
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<tr>
<td>59 -&gt; 67</td>
<td>-0.12921</td>
<td></td>
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<tr>
<td>66 -&gt; 67</td>
<td>0.64946</td>
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This state for optimization and/or second-order correction.

Copying the excited state density for this state as the 1-particle RhoCl density.

<table>
<thead>
<tr>
<th>Excited State 2: Singlet-B2</th>
<th>2.9485 eV</th>
<th>420.50 nm</th>
<th>f=0.0006</th>
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<tr>
<td>57 -&gt; 67</td>
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<td>64 -&gt; 67</td>
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<td>65 -&gt; 67</td>
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<table>
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<tr>
<th>Excited State 3: Singlet-A2</th>
<th>3.0145 eV</th>
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<th>Excited State 4: Singlet-A1</th>
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<table>
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<table>
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<th>Excited State 6: Singlet-B2</th>
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Energy calculations on parallel and perpendicular structures as per Hoffmann et al.\textsuperscript{14}

Repeated attempts to locate a parallel isomer on the singlet potential energy surface using both B3LYP/Lanl2dzp and B3LYP/Tzvp model chemistries failed. However the semiempirical approach used by Hoffmann was used to estimate the energy of this species and this was compared to the energy of the optimized perpendicular structure at the B3LYP/Tzvp level. The results are outlined in the following table.

Based on semi empirical Calculations as per Hoffmann

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<thead>
<tr>
<th></th>
<th>a.u.</th>
<th>Joules</th>
<th>kJ mol(^{-1})</th>
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<th>nm</th>
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Coordinates used in calculation of energy
Perpendicular

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Parallel (using semi empirical approach of Hoffmann$^{14}$)

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Bibliography

